A COMPREHENSIVE TREATISE ON INORGANIC AND THEORETICAL CHEMISTRY

VOLUME VIII

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Revised and Edited by G. D. Parkes, M.A., D.Phil., in collaboration with J. W. Mellor, D.Sc., F.R.S.
With numerous Illustrations.

A COMPREHENSIVE TREATISE ON

INORGANIC AND THEORETICAL CHEMISTRY

BY

J. W. MELLOR, D.Sc., F.R.S.

VOLUME VIII

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Dedicated

TO THE

PRIVATES IN THE GREAT ARMY
OF WORKERS IN CHEMISTRY

THEIR NAMES HAVE BEEN FORGOTTEN
THEIR WORK REMAINS

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ABBREVIATIONS

aq. = aqueous
atm. = atmospheric or atmosphere(s)
at. vol. = atomic volume(s)
at. wt. = atomic weight(s)
T° or °K = absolute degrees of temperature
b.p. = boiling point(s)
θ° = centigrade degrees of temperature
coeff. = coefficient
conc. = concentrated or concentration
dil. = dilute
eq. = equivalent(s)
f.p. = freezing point(s)
m.p. = melting point(s)
mol(s) $= \begin{cases}\text{gram-molecule(s)}\\ \text{gram-molecular}\end{cases}$
mol(s). $= \begin{cases}\text{molecule(s)}\\ \text{molecular}\end{cases}$
mol. ht. = molecular heat(s)
mol. vol. = molecular volume(s)
mol. wt. = molecular weight(s)
press. = pressure(s)
sat. = saturated
soln. = solution(s)
sp. gr. = specific gravity (gravities)
sp. ht. = specific heat(s)
sp. vol. = specific volume(s)
temp. = temperature(s)
vap. = vapour

In the **cross references** the first number in clarendon type is the number of the volume ; the second number refers to the chapter; and the succeeding number refers to the "§," section. Thus **5**. 38, 24 refers to § 24, chapter 38, volume 5.

The oxides, hydrides, halides, sulphides, sulphates, carbonates, nitrates, and phosphates are considered with the basic elements ; the other compounds are taken in connection with the acidic element. The double or complex salts in connection with a given element include those associated with elements previously discussed. The carbides, silicides, titanides, phosphides, arsenides, etc., are considered in connection with carbon, silicon, titanium, etc. The intermetallic compounds of a given element include those associated with elements previously considered.

The use of **triangular diagrams** for representing the properties of three-component systems was suggested by G. G. Stokes (*Proc. Roy. Soc.*, **49**. 174, 1891). The method was immediately taken up in many directions and it has proved of great value. With practice it becomes as useful for representing the properties of ternary mixtures as squared paper is for binary mixtures. The principle of triangular diagrams is based on the fact that in an equilateral triangle the sum of the perpendicular distances of any point from the three sides is a constant. Given any three substances *A*, *B*, and *C*, the composition of any possible combination of these can be represented by a point in or on the triangle. The apices of the triangle represent the single components *A*, *B*, and *C*, the sides of the triangle represent binary mixtures of *A* and *B*, *B* and *C*, or *C* and *A*; and points within the triangle ternary mixture. The compositions of the mixtures can be represented in percentages, or referred to unity, 10, etc. In Fig. 1, pure *A* will be represented by a point at the apex marked *A*. If 100 be the

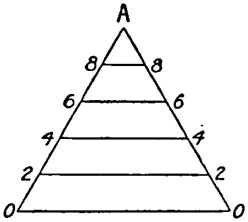

Fig. 1.

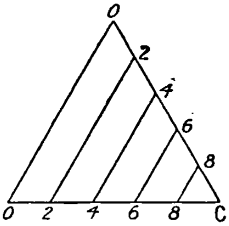

Fig. 2.

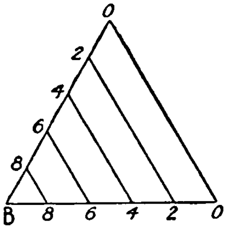

Fig. 3.

standard of reference, the point *A* represents 100 per cent. of *A* and nothing else; mixtures containing 80 per cent. of *A* are represented by a point on the line 88, 60 per cent. of *A* by a point on the line 66, etc. Similarly with *B* and *C*—Figs. 3 and 2 respectively. Combine Figs. 1, 2, and 3 into one diagram by superposition, and Fig. 4 results. Any point in this

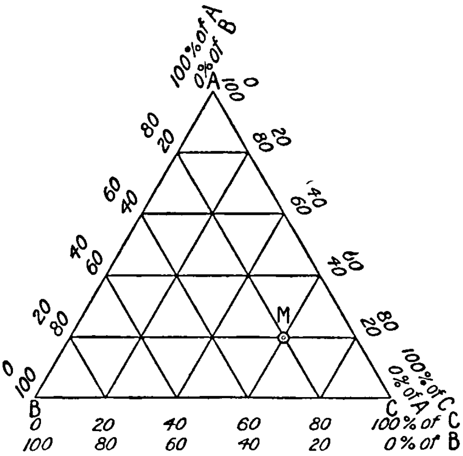

Fig. 4.—Standard Reference. Triangle.

diagram, Fig. 4, thus represents a ternary mixture. For instance, the point *M* represents a mixture containing 20 per cent. of *A*, 20 per cent. of *B*, and 60 per cent. of *C*.

CHAPTER XLIX

NITROGEN

§ 1. The Composition of the Atmosphere

> There are, I believe, few maxims in philosophy that have laid firmer hold upon the mind than that air, meaning atmospherical air (free from various foreign matters, which were always supposed to be dissolved, and intermixed with it), is a simple elementary substance, indestructible and unalterable, at least as much so as water is supposed to be.—J. PRIESTLEY.
>
> The air contributes to so great a number of chemical phenomena, by the combinations which it forms, that it is important to have a precise idea of the parts which compose it, and of the proportions in which its elements are found.—C. L. BERTHOLLET.

THE view of the ancient Greek philosophers in regarding air as one member of their quaternary system of elements; the history of the recognition of gases; the discovery that air has weight and exerts a pressure; and the discovery that air contains two dominant elements—oxygen and nitrogen—have been all discussed in the first volume of this work. M. E. Chevreul[1] wrote *sur les manières diverses dont l'air a envisagé dans ses relations avec la composition des corps*. In the eighteenth century, the evaporation of water into the atmosphere, and the condensation of water from the atmosphere, seem to have been an adequate proof of the mutual convertibility of air and water. This hypothesis was advocated by J. B. van Helmont, and it has been previously described (**1.** 3, 7). R. Boyle inclined to the same belief. Isaac Newton said that " heat converts water into vapour which is a kind of air "; and J. F. de Machy, and J. T. Eller held similar ideas. J. A. de Luc also said that electricity converts water vapour into common air, and this again into water; and he added that only in this way is it possible to explain the formation of clouds.

In a letter to R. Boyle[2] in 1678, Isaac Newton supposed that atmospheres of æther surrounded the particles of bodies which produce *cohesion*, varying with the distances, at great distances; and repulsion, at smaller distances; and added:

> The particles of vapour, exhalations, and air do stand at a distance from one another, and recede from one another as the pressure of the incumbent atmosphere will let them; for I conceive the confused mass of vapours, air, and exhalations which we call the atmosphere, to be nothing else but the particles of all sorts of bodies of which the earth consists, separated from one another and kept at a distance by the said principle.

In the seventeenth century, Robert Boyle also said:

> The air is a confused aggregate of effluviums from such differing bodies, that, though they all agree in constituting by their minuteness and various motions one great mass of matter, yet perhaps there is scarcely a more heterogeneous body in the world.

These words forcibly impress the fact that air is a mixture of several different gases—oxygen and nitrogen along with much smaller quantities of ammonia, and other nitrogen compounds; hydrogen; hydrocarbons; hydrogen dioxide; carbon dioxide; sulphur compounds; organic matter; chlorides; ozone; water vapour; and the noble or inert gases—argon, helium, krypton, neon, and xenon. The more carefully the composition of the atmosphere is examined, the more do we realize the application of Boyle's words.

Suspended solids in the form of **dust** are also common in air; thus, the outside air in London contains from 80,000 to 116,000 particles per c.c., while inside a room as many as 2,000,000 per c.c. have been counted. The air over the Pacific Ocean has been reported to have 280 to 2200 per c.c. The dust content of the atmosphere has been examined by H. H. Kimball and I. F. Hand, etc. A portion of the dust appears to be of meteoric or extra-terrestrial origin. A. E. Nordenskjöld,[3] and G. Tissandier found a dark brown dust on snow, etc., and it contained constituents like nickel, iron, phosphides, etc. A. von Lasaulx found no free iron in some dust collected at Catania; but he did observe the presence of quartz, mica, felspar, magnetite, augite, and diatoms. G. Tissandier found silica, calcium carbonate, alumina, iron chlorides and sulphates, and ammonium nitrate in atmospheric dust collected on snow. For two or three years after the eruption of Krakatoa in 1883; after the eruption of Mount Pelée and Santa Maria in 1902; and after the eruption of Katmai in 1912, a reddish-brown corona was sometimes observed as if it were around the sun. The phenomenon, known as *Bishop's ring*, was produced by the diffraction of sunlight by particles of volcanic dust in the upper regions of the atmosphere. The phenomenon was discussed by J. M. Pernter, and W. J. Humphreys. According to J. Aitken, dust of cosmic or terrestrial origin furnishes nuclei about which drops of rain are formed (**1.** 9, 6). F. O. Anderegg and K. B. McEachron showed that the fog formed when air containing ozone is passed through an absorbent soln., is chiefly caused by hygroscopic nitrogen pentoxide. According to J. J. Nolan:

> The chief evil of a polluted atmosphere is not the æsthetic horror of the smoke canopy, the grimy buildings and the stunted vegetation. It is not even the inspiration of dirty air—even though in the course of twenty-four hours of a heavy smoke fog, the dweller in London breathes in 500,000,000,000 particles of suspended matter. The real crime is the cutting off of sunlight.

The dust which is carried down with rain, hail, or snow has been analyzed by many. W. Stark, A. F. Wiegmand, W. L. Zimmermann, R. Brandes, C. Bertels, J. D. Bohlig, etc., noted the presence of calcium salts—chiefly sulphate—in rain-water; J. Girardin, in hail-stones; and A. F. Wiegmand, in snow-water. The last-named also noted the presence of phosphates in atm. dust—*vide infra,* chlorides, etc. A. Ditte, and W. N. Hartley and H. Ramage have discussed the occurrence of metals as well as meteoric dusts in the atmosphere.

Various kinds of **micro-organisms,** spores, etc., abound in the lower strata of the atmosphere. These may cause putrefactions, fermentations, and pathological phenomena of great hygienic importance. In 1744, G. Berkeley said:

> Nothing ferments, vegetates, or putrefies without air, which operates with all the virtues of the bodies included in it. The air, therefore, is an active mass of numberless different principles, the great sources of corruption, and generation; on the one hand, dividing, abrading, and carrying off the particles of bodies—that is, corrupting or dissolving them—on the other, producing new ones into being, destroying and bestowing forms without intermission. The seeds of things seem to be latent in the air, ready to pair and produce their kind whenever they light on a proper matrix. The extremely small seeds of ferns, mosses, mushrooms, and some other plants are concealed and wafted along in the air, every part whereof seems replete with seeds of one kind or other. The whole atmosphere seems alive. There is everywhere acid to corrode, and seed to engender.

The purification of air from matters in suspension has been discussed by L. Pasteur, J. Tyndall, E. T. Chapman, P. Miquel, W. Spring, F. Schulz, etc. Air may be freed from dust particles, etc., in suspension by filtration through biscuit earthenware, asbestos, or cotton wool. When a beam of sunlight is passed through unfiltered air, it reveals a multitude of motes constantly in motion. Lucretius, in his *De natura rerum* (**2.** 113, 60 B.C.), has given a very vivid description of the phenomenon. With filtered air, there is no such effect, and J. Tyndall said that such air is *optically empty.* F. O. Rice showed that in a number of reactions—*e.g.* the oxidation of soln. of sodium arsenite or sulphite, the decomposition of hydrogen dioxide, etc.—the suspended dust in air acts as a catalytic agent.

The oxygen-nitrogen ratio.—Some of the early workers believed that the proportion of oxygen and nitrogen in air varied with respect to place and time, as well as with the state of the weather. The analyses of C. W. Scheele,[4] A. L. Lavoisier, H. Cavendish, J. Dalton, J. L. Gay Lussac and F. H. A. von Humboldt, H. Davy, J. Priestley, and N. T. de Saussure rendered it highly probable that no sensible difference is to be found in the proportions of these two elements in air collected in different localities, and this is confirmed by analyses conducted more rigorously, with all known refinements. As C. L. Berthollet recognized in 1803, it appears that the variations reported by the early chemists were solely due to the uncertain action of the absorbents employed for removing oxygen from a mixture of that gas with nitrogen—*vide* the preparation of nitrogen.

In order to obtain a thorough knowledge of a great number of phenomena, said C. L. Berthollet,[5] it is important to ascertain, with all precision that can be attained, what are the proportions of oxygen and nitrogen which enter into the composition of the atm. A. Leduc calculated the composition of air from the sp. gr. of oxygen and nitrogen referred to air unity. Air may be analyzed gravimetrically or volumetrically. Historically, volumetric methods were developed before the gravimetric. In the gravimetric processes, the dried air freed from carbon dioxide is passed over hot copper (J. B. A. Dumas and J. B. J. D. Boussingault), or heated reduced iron (C. Brunner). The gravimetric analysis of air was made by C.Brunner in 1833. N. Laskowsky, and B. Verver, in 1843, weighed the oxygen absorbed by dry phosphorus, and measured the vol. of the nitrogen. J. B. A. Dumas and J. B. J. D. Boussingault absorbed the oxygen by heated copper, weighed before and after the absorption; the nitrogen was collected and weighed. They found that the ratio of the amount of oxygen in air is to that of the nitrogen as 3·682 : 12·373, that is as 22·92 : 77·08. As a mean of six determinations they obtained 23·005 grms. of oxygen per 76·996 grms. of nitrogen. The gravimetric process is very exact. The error need not exceed 0·00001th part of the whole; but the experiment requires special apparatus, and occupies much time. A similar method was used by J. S. Stas, J. C. G. de Marignac, B. Lewy, H. St. C. Deville and L. Grandeau, etc.

In volumetric processes, the oxygen is usually removed from the nitrogen by absorbents which should not disengage any gas, and which should have no action on the residual nitrogen. F. Fontana, 1774, and M. Landriani, 1775, investigated the subject, and the latter first applied the term *eudiometer* to the instrument devised by the former. J. Priestley, and C. W. Scheele, almost simultaneously, determined the quantitative composition of air, but the latter, in 1778, first attempted a systematic study of the composition of air over extended periods of time. He absorbed the oxygen by exposing a confined vol. of air to a mixture of iron filings with half its weight of powdered sulphur; he found this mixture to be more satisfactory than a soln. of potassium sulphide or calcium polysulphide later employed by A. de Marti, L. B. G. de Morveau, J. F. Berger, A. Henderson, J. L. Gay Lussac, F. C. Achard, J. de Fontanelle, J. Dalton, and M. P. Moyle. In J. Priestley's method of analysis, nitric oxide was gradually added to a measured vol. of air, in the presence of alkali-lye; the nitrogen peroxide formed by the union of nitric oxide and oxygen was absorbed by the liquid. The residual nitrogen was measured. This method of analysis was used a great deal about the beginning of the nineteenth century. Thus, F. Fontana, M. Landriani, J. H. de Magellan, J. Dalton, A. L. Lavoisier, N. T. de Saussure, J. A. Wanklyn and E. T. Cooper, J. Ingenhousz, J. G. S. von Breda, J. A. Scherer, D. A. Kreider, A. de Marti, F. H. A. von Humboldt, etc., employed this method; and H. Cavendish is said to have made over 500 analyses by this method before 1790. A. Seguin, and J. F. Berger discussed the errors of the method. D. A. Kreider passed a mixture of air and nitric oxide through a soln. of hydriodic acid, and determined, by titration, the iodine liberated. L. W. Winkler, and G. W. Chlopin determined the oxygen by treating air with manganous oxide in the presence of a soln. of potassium iodide, and determined the iodine by titration.

H. Davy, and W. Allen and W. H. Pepys employed a soln. of ferrous sulphate sat. with nitric oxide. A. Dupasquier removed the oxygen by shaking a confined vol. of air with freshly precipitated ferrous or manganous hydroxide; L. L. de Koninck, C. Brunner, and W. Flight, ferrous hydroxide; C. W. Scheele, finely divided iron, etc.; N. T. de Saussure, finely divided lead, or copper turnings moistened with sulphuric or hydrochloric acid; N. T. de Saussure, lead-waste; M. Rosenfeld, burning plumbiferous tin-foil; W. Bolton, aluminium amalgam; E. Ebermayer, A. T. Kupffer, H. A. von Vogel, L. Spallanzani, G. A. Giobert, J. B. Biot, H. E. Watson, P. Configliachi, J. F. Berger, G. F. Parrot, C. L. Berthollet, A. L. Lavoisier, A. de Marti, F. C. Achard, A. Seguin, J. J. Berzelius, A. von Baumgartner, A. Magnus-Levy, F. A. C. Gren, F. Laulanie, W. Hempel, and A. Leduc, phosphorus; S. Dumoulin, J. B. J. D. Boussingault, E. Turner, and A. F. E. Degen passed the air admixed with hydrogen over spongy platinum; and W. R. Grove found an electrically heated wire acted as well as spongy platinum. J. von Liebig, J. Schiel, C. Speck, R. A. Smith, F. G. Benedict, W. O. Atwater and F. G. Benedict, I. Macagno, J. S. Haldane, A. Krogh, A. Pécoul, A. Jaquet, H. Reboul, R. Stähelin, A. Gigon, A. Durig and N. Zuntz, K. Sondén, F. C. Calvert, S. Cloez, J. B. J. D. Boussingault, W. Hempel, and B. Tacke, absorbed the oxygen by shaking the air with an alkaline soln. of pyrogallol; soln. of tannic and gallic acids were also found to be good oxygen absorbents. An ammoniacal soln. of cuprous chloride has been tried by C. W. Scheele, D. R. T. Munoz de Luna, T. Schlösing, and M. P. L. M. Doyere, as an oxygen absorber; and a hydrochloric acid soln. of chromous chloride, by F. O. von der Pfordten, H. Moissan, N. H. Hartshorne and J. F. Spencer, R. P. Anderson and J. Riffe, W. Manchot and J. Herzog, and W. Hempel. L. G. de St. Martin, and O. Pettersson and A. Högland employed a soln. of sodium hyposulphite for absorbing oxygen—*vide* also the work of C. Brunner, and N. Dumoulin.

The methods employed by A. L. Lavoisier are only rough approximations. W. Hempel's method, with an absorption pipette, charged with sticks of phosphorus, gives very fair results. The air is first measured in a burette, then transferred to the pipette where the oxygen is absorbed, and transferred back to the burette for re-measurement. If the absorption pipette be charged with a soln. of pyrogallol in alkali-lye, the alkaline soln. becomes dark brown, almost black, as oxygen is absorbed. The explosion process may also be employed. This was devised by A. Volta in 1774, and tested by H. Cavendish in 1784. The method can give very accurate results. It was used by R. Bunsen, P. von Jolly, R. F. Marchand, W. Henry, J. F. Berger, A. R. Leeds, S. F. Hermbstädt, W. J. Russell, R. D. Thomson, C. W. Hinman, J. Dalton, H. V. Regnault and J. A. Reiset, E. Frankland and W. J. Ward, E. W. Morley, J. Geppert, A. Muntz and E. Aubin, T. Schlösing, M. Schaternikoff and J. Setschenoff, A. F. Samojloff and A. Judin, etc.

Analyses by J. S. Stas, J. C. G. de Marignac, B. Lewy, J. J. Berzelius, C. Brunner, A. Muntz and E. Aubin, M. Breslauer, B. Verver, R. Bunsen, and H. V. Regnault showed, as the last-named expressed it, that the oxygen and nitrogen in atm. air in temperate climes is approximately constant because the oxygen content was found to vary only between 20·9 and 21·0 per cent.; but in hot countries, the proportion of oxygen may fall as low as 20·3 per cent. On the other hand, P. von Jolly, E. W. Morley, A. R. Leeds, and I. Macagno believed that deviations larger than that observed by H. V. Regnault occurred. Thus, P. von Jolly found variations between 20·477 and 21·01 per cent. of oxygen in the air of München; and A. R. Leeds, between 20·821 and 21·029 in the air of New York. W. Hempel confirmed H. V. Regnault's conclusion; and U. Kreusler suggested that the incomplete desiccation of the gas in P. von Jolly's experiments explained his discrepant results. A. Krogh gave 20·948 per cent. of oxygen; 79·022, of nitrogen; and 0·030, of carbon dioxide. A small selection from the observed data is shown in Table I. The amount of atm. nitrogen varies reciprocally with the oxygen. If oxygen be high, the nitrogen will be low, and conversely. Hence, after making due allowance for differences in the methods of analysis by different men, it is clear that the **relative proportions of nitrogen and oxygen in the air are almost, but not quite, constant.** W. Hempel could detect no fluctuation in the proportion of oxygen, and the meteorological state of the air, nor could E. Ebermayer find a smaller proportion of oxygen in the air in a forest, than in the open air. E. W. Morley found that severe depressions of temp., the so-called cold-waves, are connected with the descent of air from great elevations, and the proportion of oxygen then fell from 21·006 to 20·867 per cent. by vol. A. Stock and G. Ritter found a variation of 0·75 per cent. in the oxygen content of even rural air. R. A. Smith showed that in crowded rooms, theatres, stables, cowsheds, etc., there is a shortage of oxygen. M. P. Moyle also found that the air of some Cornish mines contained as little as 14·51 per cent. of oxygen; J. F. L. Hausmann, in one of the Harz mines found 13 per cent. of oxygen; and C. H. Brockmann, an average of 19·785 per cent. of oxygen in ventilated mines of the Upper Harz. The minimum content of oxygen in air for respiration and combustion was discussed by R. A. Smith, C. Speck, F. Clowes, etc.

TABLE I.—OXYGEN CONTENT OF AIR IN DIFFERENT LOCALITIES.

Locality.	Minimum.	Maximum.	Average.	Authority.
London	20·79	21·05	20·885	R. A. Smith
Glasgow	20·85	21·01	20·909	R. A. Smith
Paris	20·913	20·999	20·960	H. V. Regnault
Manchester	20·78	21·02	20·943	R. A. Smith
Scottish Hills	20·80	20·18	20·970	R. A. Smith
Heidelberg	20·84	20·97	20·924	R. Bunsen
Bonn	20·90	20·939	20·922	U. Kreusler
Dresden	20·877	20·971	20·930	W. Hempel
Cape Horn	20·72	20·97	20·864	A. Muntz and E. Aubin
Cleveland, Ohio	20·90	20·98	20·933	E. W. Morley
Boston	20·928	20·938	20·932	F. G. Benedict

The analyses of air are usually expressed in terms of the contained oxygen and nitrogen, where the nitrogen is estimated by difference. As indicated in connection with the inert gases, Lord Rayleigh and W. Ramsay showed that the assumed nitrogen is really a complex mixture of nitrogen, argon, etc. A. Leduc estimated from the sp. gr. of the constituent gases, that the proportions of oxygen, nitrogen, and argon in air are:

	Nitrogen.	Oxygen.	Argon.
Weight	75·5	23·2	1·3
Volume	78·06	21·0	0·94

The argon was shown by W. Ramsay and M. W. Travers to be itself a complex of five inert gases—*vide* **7**. 48, 2. Air contains the following percentage proportions of these gases:

	Volume.	Weight.
Argon	0·932	1·285
Neon	0·0015	0·001
Helium	0·0005	0·00007
Krypton	0·000005	0·000014
Xenon	0·0000006	0·0000025

At sea-level, the principal gases present in dry air are very nearly in the following percentage amounts by vol.:

N_2	O_2	A	CO_2	H_2	Ne	He	Kr	X
78·03	20·99	0·93	0·03	0·01	0·0015	$0·0_35$	$0·0_55$	$0·0_66$

The average proportion of water vapour at sea-level decreases in passing from the equator to the poles, so that each of the other constituents varies proportionally. J. Hann [6] gives for the average values:

	N_2	O_2	A	H_2O	CO_2
Equator	75·99	20·44	0·92	2·63	0·02
50° N.	77·32	20·80	0·94	0·92	0·02
70° N.	77·87	20·94	0·94	0·22	0·03

There is a little evidence indicating that in the upper strata of the atmosphere, the composition of the air is very different from that in the lower strata. Air taken at sea-level contains rather a higher proportion of oxygen than air at higher altitudes. A. Wegener suggested that in the outermost regions of the atmosphere, there is a gas which he called **coronium,** or *geo-coronium.* A. Wegener estimated that the mol. wt. of coronium is 0·4; that the gas has monatomic mols.; and that the air contains about 0·00058 per cent. This gas was stated by J. Winlock to furnish a well-defined green line, 1473, in the spectrum of the aurora borealis. The same spectral lines —1474 and 5308—were reported by R. Nasini and co-workers in the spectra of some volcanic gases; by J. N. Lockyer, C. A. Young, and W. W. Campbell in the sun's corona during a solar eclipse; and by G. D. Liveing and J. Dewar, in the spectrum of the more volatile gases of the air. The evidence is circumstantial. As S. Chapman and E. A. Milne have pointed out, coronium is not likely to be present in the upper strata because, on account of its low density, it would probably not be retained by the earth. Attempts to find such a gas have failed—**7.** 48, 1.

According to W. J. Humphreys, and E. Gold, the **humidity** of the air rapidly decreases with increasing elevation to a negligibly small value at about 10 kilom.; the temp. decreases uniformly at the rate of about 6° per kilom. from an average of 11° at sea-level to —55° at an elevation of 11 kilom.; and beyond that altitude, the temp. remains constant at —55°. The relative percentages of the several gases in the air—excepting water vapour—remain constant at altitudes below 11 kilom. because of vertical convection currents; while above that elevation, the temp. changes but little with ascent, and the several gases are distributed according to their mol. wts. The air not only becomes more and more rarefied with increasing altitude, but its composition materially changes so that the heavier elements predominate in the lower strata, and the lighter elements in the higher strata.

Let b denote the barometric reading in mm.; h, the altitude in metres; θ, the temp.; and α, the coeff. of thermal expansion, approximately $\frac{1}{273}$ at 0°; then, with ordinary logarithms,

$$h=18400\log\left(\frac{760}{b}\right)(1+\alpha\theta)\quad.\ .\ .\ .\ .\ .\ .\ .\quad(1)$$

This equation is applicable to altitudes in which the composition of the atmosphere is nearly constant. The region of the earth's atmosphere which is kept approximately of a constant composition extends up to the altitudes affected by vigorous vertical convection currents. This level extends to an elevation of 11 kilom., beyond this up to the greatest altitude yet reached by sounding balloons, and presumably beyond this, the temp. changes comparatively little with change of altitude. In this isothermal region there can be but little vertical movement of the atmosphere and the several gases can distribute themselves as if each alone were present. The simple equation, $dp=pdh/H$, will therefore apply for the isothermal region, when p represents the partial press. of the gas under consideration, dh the change in elevation, and H the vertical height of the given gas, or its height, assuming its density throughout to be the same as the initial level, necessary to produce a press. p. The effect of gravity is neglected because it is so very small. The integrated equation is more adapted for numerical computation in the form:

$$\log p=\log p_0\dot{-}\frac{0{\cdot}434295}{H}(h-h_0)\quad.\ .\ .\ .\ .\ .\ .\quad(2)$$

The value of H for each gas is given by the expression $H=799D_aT/273D$, where T denotes the absolute temp.; D_a, the density of dry air, and D, that of gas in question—both at the same press. and at 0°. The percentage distribution of the gases in the atm. at different altitudes, computed by W. J. Humphreys from equations (1) and (2), is indicated in Table II; and the results are shown graphically in Fig. 1. The results for press. and temp. are supported by observations at altitudes up to 30 kilom.; and for the composition by samples of air collected by A. Wigand from heights of 9 kilom. (6 miles). The values at higher altitudes have the general uncertainty of extrapolated values. The subject has been discussed by J. H. Jeans, G. D. Hinrichs, E. W. Morley, J. Hann, E. Gold, W. J. Humphreys, J. B. A. Dumas and J. B. J. D. Boussingault, J. F. Benzenberg, K. L. Bauer, F. A. Lindemann, G. D. Hinrichs, L. Vegard, A. Rateau, F. W. Aston, etc. According to S. Chapman and E. A. Milne, the presence of hydrogen in the upper reaches of the atm. is not conclusively proved, and they showed that if it be absent, the atmosphere above 150 kilometres is almost entirely helium.

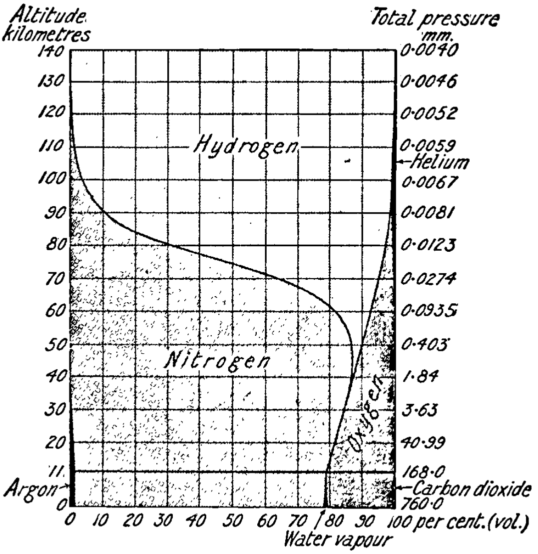

Fig. 1.—Diagrammatic Representation of the Composition of the Upper Atmosphere.

Table II.—Percentage Distribution of the Gases in the Atmosphere at Different Altitudes.

Height, kilometres.	Total pressure, mm.	Argon.	Nitrogen.	Water vapour.	Oxygen.	Carbon dioxide.	Hydrogen.	Helium.
140	0·0040	—	0·01	—	—	—	99·63	0·36
130	0·0046	—	0·04	—	—	—	99·55	0·41
120	0·0052	—	0·19	—	—	—	99·35	0·46
110	0·0059	—	0·68	0·02	0·02	—	98·77	0·51
100	0·0067	—	2·97	0·05	0·11	—	96·31	0·56
90	0·0081	—	9·86	0·10	0·49	—	88·97	0·58
80	0·0123	—	32·39	0·17	1·86	—	65·11	0·47
70	0·0274	0·03	62·04	0·20	4·74	—	32·73	0·26
60	0·0935	0·03	81·33	0·15	7·70	—	10·69	0·10
50	0·403	0·12	86·82	0·10	10·17	—	2·76	0·03
40	1·84	0·22	86·43	0·06	12·61	—	0·67	0·01
30	8·63	0·35	84·27	0·03	15·18	0·01	0·16	—
20	40·99	0·59	81·24	0·02	18·10	0·01	0·04	—
15	89·66	0·77	79·52	0·01	19·66	0·02	0·02	—
10	168·00	0·94	78·02	0·01	20·99	0·03	0·01	—
5	405	0·94	77·89	0·18	20·95	0·03	0·01	—
0	760	0·93	17·08	0·20	20·75	0·03	0·01	—

Carbon dioxide.—The existence of carbon dioxide in air was demonstrated by J. Black[7] between 1752 and 1754; ten years later by D. McBride; and in 1774, by T. Bergman. H. B. de Saussure employed lime-water as a test; and N. T. de Saussure, alkaline-lye. The latter process was used by A. F. de Fourcroy, F. H. A. von Humboldt, B. Lewy, E. Frankland, I. Macagno, etc., and P. Thénard weighed the barium carbonate produced by the action of the carbon dioxide on baryta-water.

Important memoirs were published by N. T. de Saussure, *Sur les variations de l'acide* *carbonique atmosphérique;* **J. B. A. Dumas,** *Sur l'acide carbonique normal de l'air atmosphérique ;* **W. Spring** and **L. Roland,** *Recherches sur les proportions d'acide carbonique contenues dans l'air ;* **A. Müntz** and **E. Aubin,** *Sur la proportion d'acide carbonique contenu dans l'air ;* **E. Wollny,** *Untersuchungen über den Kohlensäuregehalt der Bodenluft ;* and **E. A. Letts** and **R. F. Blake,** *The Carbonic Anhydride of the Atmosphere.*

Early reports gave remarkably high values for the proportion of carbon dioxide in atm. air. Thus, C. Girtanner gave 100–200 vols. per 10,000 vols. of air; F. A. H. von Humboldt, 50–180; J. Dalton, 6·83; and P. Thénard, 3·97. Later work reduced these figures, and in 1870, 4 vols. in 10,000 was considered to be the normal proportion in spite of the work of R. F. Marchand, who obtained 3·10; R. A. Smith, 3·36; T. E. Thorpe, and A. Krogh, 3·0; and F. Schulze, 2·86–3·01 vols. per 10,000. It was supposed that these figures were low owing to the proximity of the sea; but the determinations of J. A. Reiset, etc., indicate that the **proportion of carbon dioxide in the atmospheric air oscillates about 3 vols. in 10,000,** or, according to A. Müntz and E. Aubin, 2·82 in 10,000 for the northern hemisphere and 2·72 in 10,000 for the southern.

There is a slight increase in the proportion of carbon dioxide over *land surfaces* at night which is attributed by J. von Fodor, and E. Wollny not to the cessation of vegetable activity, but to the ground air which is normally rich in that gas. As night approaches, there is a fall of temp., and the ground air, which is then warmer than the atm., escapes and enriches the atm. with that gas. The evidence that vegetation, apart from ground air, reduces the proportion of carbon dioxide in the atm. is not very definite. The proportion of carbon dioxide in air is rather higher in towns than in the open country; but the agitation and diffusion of air by winds, etc., prevents an excessive accumulation in any part—excluding, of course, badly ventilated rooms. Thus, J. A. Reiset (1882) found 3·027 vols. of carbon dioxide per 10,000 vols. of air in Paris; and near Dieppe, 2·942 vols. These numbers may be regarded as normal. O. Haehhal found 0·4048 grm. of carbon dioxide per 100 litres of air in Berlin.

In towns, during a fog, 7 or 8 vols. of carbon dioxide in 10,000 vols. of air may accumulate; and in badly ventilated rooms, ten times the normal amount of carbon dioxide may be present. The proportion of carbon dioxide in the atm. increases during *fogs and mists;* the increase is slight in country districts, and very marked in thickly populated towns. There is generally a slight decrease in the proportion of carbon dioxide in the atm. when *rain* is falling, but there is a complication due to the effect of ground air. The general opinion is that there is an increase in atm. carbon dioxide when *snow* is falling; there is also an increase during frosty weather, and a decrease during a thaw. An increase of *wind* lessens the proportion of carbon dioxide owing to the agitation and consequent intermixture of the different air strata. At a given spot, however, the amount of carbon dioxide may vary with the nature of the surface over which the wind has previously traversed. If this happens to be water, there will probably be less carbon dioxide than with land which usually has rather more of that gas. A diminution of *pressure* should lead to an increase of carbon dioxide both over land and sea—in the former case by liberating gases from the soil, and in the latter by decomposing hydrocarbonates. A lowering of the *temperature* abates the velocity of diffusion of carbon dioxide from the lower to the upper strata of the atm.; and conversely when the temp. is raised. There are indications, more or less marked, of variations in the proportion of carbon dioxide with the *seasons.* The production and evolution of the gas from soil in early spring is checked in the summer months, and is followed in the later period of the year by an increase when vegetal activity has ceased. The effect of *clouds and sunshine* was discussed by J. A. Reiset, and A. Müntz and E. Aubin. According to W. J. Russell, the amount of carbon dioxide is below the average when the weather is fine with bright sunshine. In the country this is assumed to arise from an increase in vegetal activity, and in the city by a better circulation of air. The effect of altitude was discussed by H. B. de Saussure, N. T. de Saussure, H. and A. Schlagintweit, E. Frankland,

R. A. Smith, P. Truchot, G. Tissandier, A. Müntz and E. Aubin, E. A. Letts and R. F. Blake, E. Ebermayer, W. Marcet and A. Landriset, J. A. Reiset, and F. Schulze. Some of the earlier observers noted an increase in the proportion of carbon dioxide with moderate elevations; others, a decrease. Later observers have been unable to detect any distinct difference one way or another. For higher altitudes, *vide supra*, Fig. 1.

Attempts by C. E. Brown-Sequard and A. d'Arsonval,[8] and S. Merkel have been made to show that the depressed feeling and uneasiness experienced in crowded rooms is not solely due to the diminution of oxygen, and increase of carbon dioxide, but is rather due to the presence of a volatile organic poison in the expired air. This hypothesis was contested by A. Dastre and P. Loye, A. Russo-Giliberti and G. Alessi, D. H. Bergey, S. W. Mitchell and J. S. Billings, G. von Hofmann-Wellenhof, and K. B. Lehmann and F. Jessen. O. Wurster, and T. Cramer attributed the injurious effects to the presence of nitrates.

Moisture.—J. B. Porta[9] condensed moisture from the atmosphere on the walls of a glass vessel containing a freezing mixture. The average amount of moisture, aqueous vapour, in air is rather less than one per cent. by vol.; it may reach 4 per cent. in humid climes. The actual amount of aq. vapour air can carry before it is sat. depends upon the temp. The higher the temp. the greater the amount of moisture air can carry. Air is sat. with moisture when it contains all the water vap. it can retain at that temp. without condensation; if the air is partially sat., it will tend to become sat. by absorbing moisture. The heat required to vaporize the water may be supplied directly by the water being vaporized; or by objects in contact with the water. The variations in the proportion of water in the atmosphere are responsible for the phenomena classed as *weather*. The way it enters the atmosphere, the forms in which it is made visible, and the manner in which it is precipitated from the atmosphere, are discussed in books on meteorology. H. Kohler has discussed the form of the water drops in fogs, basing his observations on the coronæ of fogs and clouds. Even down to −28°, the drops in fogs are spherical drops, and are not crystalline.

The amount of moisture in milligrams per litre in air sat. with water vap. has been calculated by H. C. Dibbits from the vap. press. tables of G. Magnus, H. Ebert, and H. V. Regnault. The results by the latter are shown in Table III. Atm. air is never dry, and it is rarely sat. even during a heavy rain shower. According to J. H. Poynting, and G. N. Lewis, the quantity of moisture in sat. air depends both on the temp. and on the press. Air under press., in contact with liquid water, will take up more moisture at high than at low press. Air seldom contains less than 75 per cent. of the amount which it is capable of holding; but much depends on the local conditions—*e.g.*, in the Libyan desert the air contains but 9 per cent. of the possible amount of moisture.

TABLE III.—WEIGHT OF WATER IN SATURATED AIR FROM −20° TO 40° (MILLIGRAMS PER LITRE).

Temp. °C. × 10	0°	1	2	3	4	5	6	7	8	9
−2	1·058	—	—	—	—	—	—	—	—	—
−1	2·299	2·147	1·988	1·839	1·701	1·571	1·450	1·342	1·241	1·146
−0	4·868	4·527	4·201	3·898	3·617	3·355	3·112	2·886	2·676	2·481
0	4·868	5·209	5·570	5·953	6·359	6·789	7·246	7·730	8·242	8·784
1	9·356	9·961	10·600	11·275	11·987	12·788	13·531	14·366	15·246	16·172
2	17·147	18·173	19·252	20·386	21·578	22·830	24·144	25·524	26·971	28·488
3	30·079	31·746	33·492	35·320	37·232	39·232	41·324	43·511	45·797	48·185
4	50·677	—	—	—	—	—	—	—	—	—

The **absolute humidity** of air refers to the mass of water vapour actually present in unit vol., and it is determined by passing a known vol. of air over a suitable drying agent—calcium chloride, phosphorus pentoxide, etc. (**1.** 7, 2)—and finding the increase in the weight of the desiccating agent. The results can be expressed in milligrams per litre, grams per cubic metre, etc. The absolute humidity is also expressed in terms of the press. exerted by the water vapour per unit area—dynes per sq. cm., millimetres of mercury, etc.—since the press. exerted by any component in a uniform mixture of gases is to the total press., as the number of its mols. per given vol. is to the total number of mols. in the mixture. Hence, the vap. press. varies directly as the vapour density, or mass per unit vol. The two definitions of absolute humidity are therefore eq. for any assigned temp. The term **specific humidity,** occasionally used, refers to the weight of water vapour in unit weight of moist air. The term **relative humidity,** at any given temp., refers either to the ratio of the actual to the saturation quantity of water vapour per unit vol.; or to the ratio of the actual to the saturation press. of water vapour. The **dew-point** is the temp. at which without change of press., the air is saturated; it is the temp. at which the saturation press. is the same as the existing vap. press. of the water. If θ_s° be the dew-point, when the saturation or maximum vap. press. is f_s; and the vap. press. at θ is f; the relative humidity is f/f_s. Again, let p mm. denote the barometric press.; θ°, the temp.; and f, the vap. press.; then, if θ° be the temp. of a well-ventilated wet-bulb thermometer, and f_s the saturation vap. press. at θ_1°, then, with temp. expressed in °C, and press. in mm. of mercury, the vap. press. f, at θ°, is given by the empirical formula $f=f_s-0{\cdot}000660p(1+0{\cdot}00115\theta_1)(\theta-\theta_1)$. Hence, when f is known, the relative humidity can be calculated. According to J. Dalton's law, $P=p+f$, where P represents the observed barometric press.; p, the corresponding press. of dry air; and f, the press. of the water vapour. This law is applicable when the air is sat.; if the air be not sat., then if h denotes the relative humidity (per cent.), $P=p+hf$.

Ozone and hydrogen dioxide.—Probably these substances are formed by electrical discharges in the atm. as indicated in connection with the formation of these substances (**1.** 14, 2 and 8). There is probably sufficient ozone in the earth's atm. to be of importance with both the incoming and the outgoing radiation. The magnitude of solar energy consumed by ozone is uncertain because the amount of this gas in the air is also unknown. Ozone in moist air at ordinary temp. soon reverts to oxygen so that only traces of it are found in the lower atmosphere. On the contrary, in the upper atmosphere where there is but little moisture, and where the temp. approximates to −55°, ozone is far more stable; the extreme ultra-violet rays emitted by the sun, when passed into cold dry oxygen, convert much of it into ozone so that, according to H. Henriet and M. Bonyssy,[10] and W. J. Humphreys, appreciable amounts of this gas are presumably present in the upper atmosphere. J. N. Pring estimates the ozone in the upper atmosphere to be eq. to a layer of pure gas 4·2 cms. thick, at normal temp. and press. The upper atmosphere is relatively richer in ozone than air from lower levels. E. Ladenburg and E. Lehmann have measured the absorption spectrum of ozone down to $\lambda=12\mu$; A. K. Angström discovered solar bands $\lambda=4{\cdot}7\mu$ and $\lambda=9{\cdot}5\mu$ respectively, and the observed limit of the solar spectrum appears to be fixed by an ozone band of extraordinary absorptive power whose maximum occurs at about $\lambda=0{\cdot}254\mu$—*vide* Fig. 2. H. N. Holmes found the proportion of ozone in atm. air to be greater in winter than in summer.

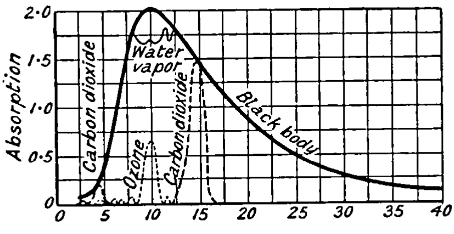

FIG. 2.—Water vapour, carbon dioxide, and ozone absorption at 14·2°.

Hydrogen and combustible carbon compounds.—The occurrence of hydrogen in atm. air is derived from the sources indicated in connection with that gas—*vide* the occurrence of hydrogen. G. D. Liveing and J. Dewar [11] found hydrogen in distilling liquid air. Lord Rayleigh estimated that one vol. of hydrogen is present in 30,000 vols. of air. G. Claude found less than one part of hydrogen in a million parts of air. N. T. de Saussure found hydrocarbons in atm. air, and this was confirmed by J. B. J. D. Boussingault. B. Verver found that the air of Lyons contained one vol. of hydrocarbon in 10,000 vols of air. W. Omeliansky made some observations on the occurrence of methane in air. A. Müntz and E. Aubin reported the presence of methane, carbon monoxide, etc., in atm. air; and A. Müntz found traces of alcohol in the air, and in rain-water. F. C. Phillips could detect no hydrogen in atm. air; but A. Gautier found that the air in the neighbourhood of towns contains variable quantities of combustible carbon compounds, but only minute traces of these gases can be detected in the air of mountainous regions, and in sea-air. For instance, the air of Paris contains per 100 litres—19·4 c.c. of free hydrogen, 12·1 c.c. of methane, 1·7 c.c. of benzene and related hydrocarbons, and 0·2 c.c. of carbon monoxide with traces of olefines and acetylenes. A. Leduc, and Lord Rayleigh considered that A. Gautier's estimate for hydrogen is probably rather high. H. Henriet found 2 to 6 grms. of formaldehyde per 100 cubic metres of air. The presence of hydrocarbons explains the oleaginous character of the deposits which form on roofs, leaves of trees, etc., in towns. W. L. Zimmermann and others have reported on various forms of organic matter in atm. air, or in rain-, hail-, or snow-water. According to A. Gautier, the hydrogen in the atm. may be derived, not only from volcanic action and other well-known sources, but also from the action of water on ancient granitic rocks at temp. considerably below a red-heat. Granite from the interior of a fairly large block, powdered in an atm. of carbon dioxide and afterwards heated with dil. acids at 100° or with water alone at 280°, yields a considerable quantity of gas, consisting mainly of hydrogen, together with hydrogen sulphide, ammonia, carbon dioxide, nitrogen, and traces of unsaturated hydrocarbons, and sometimes traces of methane. The hydrogen and the ammonia are probably due to the action of water on nitrides, chiefly iron nitrides, although possibly some of the hydrogen may be derived from its action on carbides.

Chlorine and iodine compounds.—Rain near the sea brings down a certain amount of chloride derived from the sea-water. The proportion of salt in the air is greatest near the sea-shore, and diminishes rapidly inland from the coast. In 1822, J. C. Driessen wrote a memoir: *De acidi muriatici præsentia in aëro atmosphærico.* Observations on the occurrence of hydrochloric acid or rather chlorides in the atmosphere were made by A. Vogel,[12] M. Roubaudi, W. Meissner, J. von Liebig, and W. A. Lampadius. J. Dalton found that at Manchester, 10,000 kgrms. of rain-water contain more than a kilogram of sodium chloride. R. A. Smith made observations on the chlorides in air in the vicinity of Manchester. R. Brandes obtained 312 kgrms. of solid matter from a million kilograms of rain-water, and found that the residue contained potassium, sodium, manganese, iron, calcium, ammonium, and magnesium chlorides, carbonates, and sulphates, and organic matters. J. I. Pierre stated that at Caen, a hectare of land receives annually by rain sodium chloride, 37·5 krgms.; potassium chloride, 8·2 kgrms.; magnesium chloride, 2·5 kgrms.; and calcium chloride, 1·8 kgrms. J. A. Barral estimated that every hectare at Paris receives the eq. of 13 kgrms. of chlorine by rain annually; and E. Kinch found, as an average of twenty-six years' observations at Cirencester, that 36·1 lbs. of sodium chloride per acre per annum were brought to the earth with the rain. The amount of "wind-borne" sea salt is greatest when the wind blows from the sea. Observations were also made by G. Bellucci, G. C. Whipple and D. D. Jackson, A. Bobierre, E. L. Peck, N. H. J. Miller, J. Pirovaroff, J. B. Harrison and J. Williams, G. Gray, E. S. Richards and A. T. Hopkins, B. Artis, J. de Fontenelle, N. Passerini, J. B. Lawes and co-workers, and A. Gautier. Numerous other observations have been made from the agricultural point of view in studying the saline substances carried to the soil from the atm. by rain. F. W. Clarke has compiled Table IV showing the amount of chlorides precipitated on land by rain. The results are expressed in pounds per acre per annum.

TABLE IV.—CHLORIDES BROUGHT TO THE SURFACE OF THE EARTH BY RAIN.

Locality.	Chlorine.	Sodium chloride.
Cirencester, England	—	36·10
Rothamsted, England	14·40	24·00
Perugia, Italy	—	37·95
Ceylon	180·63	—
Calcutta	32·87	—
Madras	36·37	—
Odessa, Russia	17·00	—
Barbados	116·98	—
British Guiana	129·24	195·00
New Zealand	61·20	—

According to A. Gautier, at 15°, a quantity of chlorine eq. to 0·022 grm. of sodium chloride per cubic metre of air represents the maximum quantity of salt which sea air can retain in suspension. In 1877, F. Posepny, and E. Tietze discussed the atmospheric circulation of salt, and tried to show that the sodium chloride of inland waters is derived from this source. W. Ackroyd, and A. Müntz advocate this view, and, added the latter, without this circulation of salt, the land would not be replenished, and living beings would suffer. E. Dubois estimated that about 6,000,000 kgrms. of salt are annually precipitated by rainfall on two provinces of Holland. These *cyclic salts*, or wind-borne salts, play a distinct part in the economy of nature. R. A. Smith showed that free hydrochloric acid derived from manufacturing operations is sometimes found in air of towns. A. Gautier found that less than 0·002 mgrm. of free iodine, or gas containing iodine, is present in about 4000 litres of dust-free air of Paris; similarly, the dust-free air from the sea, forest, or mountain districts contains no appreciable quantity of iodine. No iodine in the form of soluble salts is present in the small particles of dust in the air. The air from Paris and from the sea contain respectively 0·0013 mgrm. and 0·0167 mgrm. of iodine in 1000 litres. This iodine is probably present in small vegetable organisms suspended in the air. It is detected by filtering the air through glass wool, and afterwards fusing the latter with potash. Although the presence of iodine as a normal constituent of the atmosphere was denied by F. Garrigou, S. Cloez, and S. de Luca, its presence was confirmed by E. Marchand, A. Chatin, A. A. B. Bussy, P. Thénard, and J. Bouis—*vide* **2.** 17, 5.

Nitrogen oxides.—In the eighteenth century, B. Ramazzini,[13] A. S. Marggraf, and T. Bergman observed that snow-water contains some vestiges of nitric acid—*vide infra*, nitric acid. As shown by F. Goppelsröder, E. Bechi, R. A. Smith, and G. Defren, the oxides of nitrogen are probably formed by electrical discharges in the atmosphere. The nitrites or nitrates obtained from atm. air are greater during thunderstorms than during ordinary rain. J. von Liebig, indeed, said that only the rain of a thunderstorm contains nitric acid, but other observers agree that nitric acid or nitrates occur more frequently. Thus, G. Defren found that water exposed undisturbed to the air absorbs nitrites there existing; and the amount so absorbed increases in almost direct proportion to the time of exposure. Free nitric acid has been reported in the atm. of tropical regions, but generally, the nitric acid is combined with ammonia. J. A. Barral estimated that 63·6 kgrms. of nitric acid fall per hectare per annum at Paris; and A. Bineau observed at Lyons 0·3 mgrm. of nitric acid per litre of rain in winter; 1·0 mgrm. in spring; 2 mgrms. in summer; and 1·0 mgrm. in autumn. According to A. Lévy, about 3 lbs. of ammoniacal nitrogen, and 1 lb. of nitric acid is returned to the earth per acre per annum with the rain. In rural districts the soil is said to receive between 4 and 6 lbs. of combined nitrogen per acre per annum from the rain. Observations on the presence of nitric acid or nitrates were also made by W. Knop, J. B. J. D. Boussingault, W. A. Lampadius, J. F. Heller, R. A. Smith, C. F. Mabery and H. Snyder,

F. Goppelsröder, A. Bobierre, E. Bechi, C. Chabrier, A. Müntz and V. Marcano, R. Warington, J. B. Harrison and J. Williams, J. B. Lawes and co-workers, etc. Table V was compiled by F. W. Clarke—*vide infra*—where the data are expressed in pounds per acre per annum. The occurrence of nitrous acid in air and rain was discussed by G. Chabrier, F. Goppelsröder, and L. I. de Nagy Ilosva. According to W. Hayhurst and J. N. Pring, the proportion of nitrous acid in atm. air varies from time to time, being less than 1 part in 4,000,000,000 parts of air; the proportion is greater at high than at low altitudes. The ratio of the oxides of nitrogen in the upper to that in the lower atmosphere was found to be 2·23 : 1 at 8500 ft. elevation, and 1·76 : 1 at 2600 ft. elevation.

TABLE V.—NITROGEN BROUGHT TO THE EARTH'S SURFACE BY RAIN.

Locality.	Ammoniacal.	Nitric.	Total.
Rothamsted, England	2·71	1·13	3·84
Paris	—	—	8·93
Caracas, Venezuela	—	0·516	—
Gembloux, Belgium	—	—	9·20
Barbados	1·009	2·443	3·452
British Guiana	1·006	1·886	3·541
Kansas, U.S.	2·63	1·06	3·69
Utah, U.S.	5·06	0·356	5·42
Mississippi, U.S.	—	—	3·636
New Zealand	—	—	2·08
Iceland	0·802	0·263	1·065
Hebrides	0·311	0·289	0·600

Ammonia.—In the eighteenth century, C. W. Scheele[14] noted that the mouths of bottles containing acids were encrusted with ammonium salts after standing in a room for some time; and J. B. A. Chevallier found that ammonium salts—carbonate, nitrate, nitrite, sulphide, and acetate—were present in the air of Paris. Other observations were made by N. T. de Saussure, T. Bergman, R. Brandes, J. von Liebig, J. I. Pierre, A. Schöyen, W. L. Zimmermann, C. S. Collard de Martigny, E. N. Horsford, C. R. Fresenius, G. Ville, B. Artis, E. L. Peck, P. Truchot, N. Gräger, H. T. Brown, F. Goppelsröder, A. Lévy, G. Kemp, J. A. Wanklyn, W. Knop, E. Bechi, A. Schlösing, A. Müntz and co-workers, H. T. Brown, J. B. Lawes and co-workers, J. B. Harrison and J. Williams, and R. Warington. According to M. Faraday, if china clay be heated to redness and exposed to air for a week, it yields a considerable quantity of ammonia when heated again, which is not the case when the clay has been kept in a closed vessel. The ammonia in the atmosphere is largely a product of organic decomposition, and it is returned to the earth by rain in the form of ammonium nitrate or nitrite, and sometimes as ammonium sulphate or chloride. Numerous observations have been made on the amount of ammonia present in atm. air, and carried down by rain-water. J. A. Barral estimated that every hectare at Paris receives annually 15·3 kgrms. of ammonia, and A. Bineau, at Lyons, 68 kgrms. J. B. J. D. Boussingault observed that the most ammonia is present in the first part of a rainfall. After some days without rain, he observed successively the following proportions of ammonia per litre:

Rain gauge	0·5	0·5–1	1–5	5–10	10–15	15–20	20–31 mm.
Ammonia	3·11	1·20	0·70	0·45	0·45	0·41	0·40 mgrms.

The proportion condensed during fogs is greater, reaching in one case 50 mgrms. of ammonia per litre. Falling snow contains a notable proportion of ammonia; the snow collected on a terrace contained 1·78 mgrms. per litre, and that collected on an adjoining garden, 10·34 mgrms. per litre. This is taken to mean that ammonia was set free from the soil and intercepted and absorbed by the snow. A. Bineau obtained 70 mgrms. per litre by the melting of a hoar frost. R. A. Smith found in

England 0·97 mgrm. per litre of rain in the country, and 5·14 mgrms. in the towns; and in Scotland, 0·53 mgrm. in the country, and 3·81 mgrms. in the town. Table V shows that ammoniacal nitrogen is usually in excess of nitric nitrogen, but the converse is true of tropical countries. The ammonia is usually collected by the acids—nitric, hydrochloric, or sulphuric—in the atmosphere and carried to earth in rain or snow.

Sulphur compounds.—Sulphuric acid and sulphates found in rain-water may be derived in part from water which is volatilized from seas, lakes, and rivers, being carried mechanically along with the vapour; or it may be formed in the air itself—*vide* sulphuric acid. Thus, G. F. Rouelle,[15] about the middle of the eighteenth century, said:

> When one steeps a well-cleaned cloth in potash-lye free from sulphuric acid, and exposes it to the air in a place free from rain and dust, the cloth becomes wet and dry alternately a great many times; at last it becomes dry and does not again become wet; the potash with which it was impregnated, is found changed into sulphate.

P. von Driessen and M. Veehof found sulphuric acid; and F. d'Arcet, and J. B. A. Chevallier, sulphur dioxide and sulphuric acid in the air of towns, and it was supposed to have been derived from the combustion of coal. R. Brandes, and J. de Fontenelle observed the presence of sulphates in the solid residue formed by the evaporation of rain-water. Alkali sulphates in contact with organic matter may be reduced to hydrogen sulphide; the same gas can be produced by the putrefaction of organic matter; and it occurs among the gases given off by volcanoes. Sulphur dioxide is emitted by volcanoes, and is produced by the combustion of coal. Hence, this gas (*q.v.*) is to be expected in the air of manufacturing districts. Thus, A. Ladureau reported 1·8 c.c. of sulphur dioxide per cubic metre in the air of Lille; and O. Haehhal found 0·003281 grm. of SO_2 per 100 litres of air in Berlin. Sulphur compounds are present in small quantities as hydrogen sulphide, sulphur dioxide, and sulphuric acid in the air of towns. The rapid oxidation of sulphur dioxide in the presence of moisture results in the formation of sulphuric acid or of the sulphates. According to R. Warington, about 17¼ lbs. of sulphuric acid are annually "poured" upon each acre of land at Rothamsted. G. H. Bailey reported a maximum of 0·0267 grm. of sulphur estimated as sulphur trioxide in the air near the surface of the ground in Manchester. J. I. Pierre showed that in the vicinity of Caen, a hectare of land receives annually by rain, sodium sulphate, 8·4 kgrms.; potassium sulphate, 8·0 kgrms.; calcium sulphate, 6·2 kgrms.; and magnesium sulphate, 5·9 kgrms. Other observations have been made by J. B. Lawes and co-workers, S. Robinet, R. A. Smith, N. H. J. Miller, G. Gray, B. Artis, and E. L. Peck.

Is air a mixture or a compound of oxygen and nitrogen?—Observations by P. A. Guye and co-workers,[16] W. J. Humphreys, E. W. Morley, etc., have shown that there is probably a very small conc. of the denser gas, oxygen, in the atm. near the surface of the earth—*vide supra*—although analyses of air collected from mountain tops, and balloons have not borne out this suspicion. The fact that the proportions of oxygen and nitrogen in air do not vary with moderate variations of altitude appears to have been mainly responsible for the belief that these gases are in a state of chemical combination. C. L. Berthollet, T. Thomson, J. Murray, and H. Davy at first "leaned towards the idea of chemical combination," and J. Gough added that if the particles of oxygen exist in the atm. independently of the particles of nitrogen, sound will be transmitted by the one gas with one velocity, and by the other gas with another velocity, so that at a sufficient distance away a sound should be heard double. The view that air is a chemical compound was persistently maintained until the advent of J. Dalton's theorems in 1801 explaining the relation of mixed gases towards one another. J. Dalton showed that "when two elastic fluids, denoted by A and B, are mixed together, there is no mutual repulsion amongst their particles, that is, the particles of A do not repel those of B, as they do one another." In the proof, it was shown that if two kinds of air are put into the same vessel with very great care, without the least agitation that might mix or blend them together, each gas diffuses uniformly throughout the other. A light gas cannot rest long on a heavier gas. Particles of one kind may offer a kind of passive resistance to the motion of the particles of the other kind, and act as temporary obstacles in the same way as the pebbles in a stream impede the flow of water (1. 4, 4). The following summarizes the main evidence :

1. The proportions of the constituents of air vary a little in different localities, but even this small variation is not found with pure chemical compounds—law of constant proportions. Hence, not all the nitrogen and oxygen are combined.

2. The atomic proportion of nitrogen and oxygen in air is as 3·77 : 1 ; this is approximately as 15 : 4. Hence, if all the nitrogen and oxygen are combined, the formula of the compound is $N_{15}O_4$, or $NO_{0·26}$, which does not fit very well with the facts summarized by the law of multiple proportions. A similar result is obtained by considering the volume-temperature relations of nitrogen and oxygen in air.

3. The characteristic physical properties (refractive index, absorption of radiant heat, etc.) of nitrogen and oxygen are modified in air only so far as obtains when nitrogen and oxygen are *mixed* in the same proportions. The properties of the two gases are not changed so much as would be expected if a chemical compound were formed. Thus, J. B. Biot found that the refractive index of air is equal to that calculated for an eq. mixture of oxygen and nitrogen ; and J. Tyndall found that the amount of heat absorbed when heat rays are allowed to pass through a column of an elementary gas is much less than is the case with compounds. Thus, air, oxygen, nitrogen, and hydrogen have nearly the same value—say unity—whereas carbon monoxide has an absorptive power of 972 ; nitric oxide, 1590 ; nitrous oxide, 1860 ; and ammonia, 5460. According to H. St. C. Deville, if a measurable physical property were different in air and in an equivalent mixture of the constituents of air, the conclusion would follow that air is a compound.

4. The constituents of air can be separated by mechanical means, *e.g.* solution in water : by atmolysis ; by allowing liquid air to vaporize, when the nitrogen distils off before the oxygen ; and J. Dewar showed that liquefied air like liquid oxygen will remain suspended to a magnet in virtue of the oxygen it contains ; there is no separation. If, however, the liquid air be solidified, the oxygen can be separated from the nitrogen by means of an electromagnet much as iron filings can be separated from brass turnings. Hence, solid air behaves like a magma whose constituents, nitrogen and oxygen, can be separated by a magnet.

5. No heat, no change of vol., or any other sign of chemical change is observed when air is made artificially by mixing the gases together in the correct proportions.

Not one of these five reasons is in itself conclusive, but all, taken together, form a long chain of circumstantial evidence which quite justifies J. W. Dobereiner's verdict : *Das atmosphärische Gase ist keine chemische Verbindungen.* Air is a mechanical mixture of nitrogen, oxygen, etc.

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§ 2. The Physical Properties of Air

Some observations on the weight of air were made at the beginning of the fourth chapter—**1**. 3, 1—of this work. J. B. Biot and F. J. Arago[1] said that the **weight of a litre** of dry air, freed from carbon dioxide, and at 0° and 760 mm., is 1·299541 grm. ; and J. B. A. Dumas and J. B. J. D. Boussingault gave 1·2995 grm. Later workers obtained rather smaller values—thus, H. V. Regnault gave 1·293187 grm. ; J. M. Crafts, 1·29349 ; P. von Jolly, 1·29383 ; M. S. Blanchard, 1·29287 ; G. Agamennone, 1·29310 ; W. Lasch, 1·293204 ; F. Kohlrausch, 1·293635 ; A. Leduc, 1·2933 ; Lord Rayleigh, 1·29327 ; and P. A. Guye, 1·2930. O. J. Broch, and J. Treuthardt made some observations on this subject. The best representative value for the weight of a litre of dry air, freed from carbon dioxide, at 0° and 760 mm., is 1·2930 grm., at sea level, and latitude 45°.

According to A. Leduc, the weight of a litre of air can vary by a milligram owing to variations in composition. There is therefore no particular advantage in weighing air to a greater accuracy than $\frac{1}{20}$th of a milligram without at the same time determining the composition of the air. For the same reason, there is no need to measure the density of other gases with respect to air to an accuracy greater than 0·0001. Accepting A. Leduc's value 0·08985 grm. for the weight of a litre of hydrogen, the **relative density** of air, referred to hydrogen unity, is 14·394 : and with Lord Rayleigh's value, 0·09001 grm. for the weight of a litre of hydrogen, the relative density of air is 14·368. W. Lasch made some observations on this subject. G. P. Baxter discussed the determination of the density of air. M. Paya and E. Moles found the normal density of the nitrogen from the air of Madrid is 1·25681 ; and the density of the air indicates a slightly higher proportion of oxygen, which is attributed to the presence of a higher proportion of ozone and argon gases than normal. A. Stock and G. Ritter found a variation of 0·13 per cent. on the density of even rural air. E. Moles added that since the normal density of air may vary as much as 0·1 per cent., the use of air as a standard for gas densities should be abandoned. A. Jaquerod and C. Borel found that the amplitude of the variations in the density of the air of Neuchâtel does not usually exceed 0·5–0·6 mgrm. The same result was found with air taken at an elevation of 2000–5000 m., but the deviation is smaller. The explanation which assumes the presence of a heavy gas is rejected and the presence of ultramicroscopic dust is suggested. Water at 4° is 773 times as heavy as a litre of air at 0° and 760 mm. The **specific gravity** of air referred to that of water is 0·0012933 with A. Leduc's data, and 0·0012932 with Lord Rayleigh's. P. A. Guye gave 0·0012928 for the best representative value ; values given by A. Leduc, Lord Rayleigh, P. A. Guye and co-workers, and F. O. Germann range from 0·0012973 to 0·0012926. The results in Table VI for the sp. gr. of dry air, with 0·04 vol. per cent. of carbon dioxide, at 760 mm., were calculated from $D=0{\cdot}00129307/(1+a\theta)$, where the constant $a=0{\cdot}0036730$ from 0°

to 50°; 0·0036715 from 0° to 100°; 0·0036704 from 0° to 150°; and 0·0036696 from 0° to 200°. A. Rateau discussed the effect of altitude on the sp. gr. of air.

TABLE VI.—SPECIFIC GRAVITY OF DRY AIR AT DIFFERENT TEMPERATURES AND 760 MM.

°C.×10	0	1	2	3	4	5	6	7	8	9
	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00
−2	13957	14013	14069	14125	14182	14240	14296	14354	14413	14472
−1	13424	13476	13527	13580	13632	13685	13739	13793	13847	13902
−0	12940	12978	13026	1307$\bar{5}$	13124	13173	13222	13272	13322	13373
+0	12940	12883	12836	12790	12743	12697	12652	12606	12561	12517
+1	12472	12428	1238$\bar{5}$	12341	12298	12255	12213	12170	12129	12087
+2	12046	12004	11964	11923	11883	11843	11803	11764	1172$\bar{5}$	11686
+3	11647	11609	11570	11533	1149$\bar{5}$	11458	11420	11383	11347	11310
+4	11274	11238	11202	11167	11132	11097	11062	11027	10958	10857
+5	10924	10981	10857	10824	10791	10758	1072$\bar{5}$	10692	10660	10628
+6	10596	10564	10532	10501	10470	10439	10408	10377	10347	10316
+7	10286	10256	10227	10197	10168	10138	10109	10080	10052	10023
+8	0999$\bar{5}$	09966	09938	09910	09882	09855	09828	09800	09773	09719
+9	09719	09692	09666	09639	09613	09387	09561	0953$\bar{5}$	09509	09484
+10	09458	09433	09408	09383	09358	09333	09308	09284	09259	09235
+11	09211	09187	09163	09139	09116	09092	09069	09045	09022	08999
+12	08976	08954	08931	08908	08886	08864	08841	08819	08797	08775
+13	08753	08732	08710	08689	08667	08646	08625	08604	08583	08562
+14	08541	08521	08500	08480	08459	08439	08419	08399	08379	08359
+15	08339	08320	08300	08281	08261	08242	08223	08204	08184	08165
+16	08147	08128	08109	08091	08072	08054	08035	08017	07999	07981
+17	07963	0794$\bar{5}$	07927	07909	07891	07874	07856	07839	07821	07804
+18	07787	07770	07753	07736	07719	07702	07685	07668	07652	07635
+19	07619	07602	07586	07570	07553	07537	07521	07505	07489	07473
+20	07457	07442	07426	07410	0739$\bar{5}$	07397	07364	07349	07333	07318
+21	07303	07288	07273	07258	07243	07228	07213	07199	07184	07169
+22	0715$\bar{5}$	07140	07126	07112	07097	07083	07069	0705$\bar{5}$	07040	07026

S. von Wroblewsky measured the sp. gr. of liquid air. U. Behn and U. Kiebitz gave for the sp. gr. of liquid air referred to water at 4°:

	−195·7°	−195°	−193°	−191°	−189°	−187°	−185°	−183°	−182·4°.
D .	0·701	0·826	0·919	0·995	1·050	1·092	1·118	1·130	1·131

A. Ladenburg and C. Krügel showed that the composition quickly changes as the liquid is exposed to the atm., and the sp. gr. changes in a corresponding way. Newly condensed air with 53·83 per cent. of oxygen had a sp. gr. 0·9951; after standing some time, it had 64·2 per cent. of oxygen, and a sp. gr. 1·029; and after standing between one and two days, it contained 93·6 per cent. of oxygen, and had a sp. gr. 1·112. Liquid air with the same composition as atm. air has a sp. gr. 0·87 to 0·90. The sp. gr., D, of liquid air at its b.p., and containing x per cent. of oxygen, is represented by $D=0·86+0·00289x$. J. K. H. Inglis and J. E. Coates found that liquid air, with y vol. per cent. of nitrogen, at 74·70° K., and a vap. press. of 100 mm. of mercury, has the following vol., v:

y .	0	1·8	13·9	37·8	59·3	86·8	98·8	100
v .	0·28332	0·28429	0·27959	0·28301	0·28200	0·28324	0·28065	0·28214

According to J. Natterer,[2] the **compressibility** of atm. air does not deviate very markedly from Boyle's law, and L. Cailletet showed that only at very high press.—up to 2790 atm.—is air a little more compressed than corresponds with that law. H. V. Regnault found the ratio p_0v_0/pv, increased from 1·001414 with $p_0=738·7$

mm. and $p=1476{\cdot}3$ mm., to 1·006619 with $p_0=11472{\cdot}0$ mm. and $p=20969{\cdot}4$ mm. P. Siljeström said that with increasing dilution, the elasticity of air is greater than that which corresponds to Boyle's law. D. I. Mendeléeff inferred that Boyle's law is equally valid for air at low and at high press.; and that as the press. is diminished air deviates more and more from the law, thus, if $pv=1$ at 650 mm. press., $pv=0{\cdot}6$ at 0·5 mm. press. V. Hemilian and co-workers found a greater compressibility than corresponds with Boyle's law for air at press. over 760 mm., and conversely for press. between 20 mm. and 650 mm. On the other hand, E. H. Amagat found that air follows Boyle's law very closely for press. between 0·001 mm. and 10·5 mm. of mercury; at 100°, air follows Boyle's law between 1 and 8 atm. press. and probably for higher press. For unit vol. of air at 1 atm. press. and 15°, he found:

p .	750	1000	1500	2000	2500	3000 atm.
v .	0·002200	0·001974	0·001709	0·001566	0·001469	0·001401

He inferred accordingly that at high press., the coeff. of compressibility of air is of the same order of magnitude as that of a liquid. The press. in atm. at which the product pv is a minimum for different temp. was found by E. H. Amagat to be:

TABLE VII.—E. H. AMAGAT'S VALUES FOR pv FOR AIR.

p Atm.	0·0°		15·70°		99·40°		200·4°	
	pv	v	pv	v	pv	v	pv	v
1	1·0000	1·000000	—	—	—	—	—	—
100	0·9730	0·009730	1·0460	0·010460	1·4030	0·014030	—	—
150	0·9840	0·006560	1·0580	0·007053	1·4310	0·009540	1·8430	0·001229
200	1·0100	0·005050	1·0855	0·005427	1·4670	0·007335	1·8860	0·009430
250	1·0490	0·004196	1·1260	0·004504	1·5110	0·006044	1·9340	0·007736
300	1·0975	0·003658	1·1740	0·003913	1·5585	0·005194	1·9865	0·006622
350	1·1540	0·003297	1·2250	0·003500	1·6085	0·004596	2·0140	0·005831
400	1·2145	0·003036	1·2835	0·003209	1·6625	0·004156	2·0960	0·005240
450	1·2765	0·002837	1·3460	0·002991	1·7200	0·003822	2·1530	0·004785
500	1·3400	0·002680	1·4110	0·002822	1·7185	0·003563	2·2110	0·004422
550	1·4040	0·002553	1·4740	0·002680	1·8440	0·003353	2·2700	0·004127
600	1·4700	0·002450	1·5375	0·002563	1·9060	0·003177	2·3300	0·003883
650	1·5365	0·002363	1·6015	0·002464	1·9670	0·003026	2·3900	0·003677
700	1·6020	0·002288	1·6670	0·002381	2·0300	0·002900	2·4515	0·003502
750	1·6690	0·002225	1·7340	0·002312	2·0930	0·002790	2·5130	0·003351
800	1·7345	0·002168	1·8000	0·002250	2·1555	0·002694	2·5750	0·003219
850	1·7990	0·002116	1·8655	0·002194	2·2180	0·002609	2·6370	0·003102
900	1·8640	0·002071	1·9300	0·002144	2·2830	0·002537	2·8000	0·003000
950	1·9280	0·002030	1·9960	0·002101	2·3490	0·002437	2·7640	0·002903
1000	1·9920	0·001992	2·0600	0·002060	2·4150	0·002415	2·8280	0·002828

	−135°	−103·5°	−78·5°	−35°	0°	16°	100°
p . .	75	139	162	151	125	104	c. 14 atm.

He calculated the compressibility coeff., $\beta=dv/vdp$ to be $0{\cdot}0_3411$ between 750–1000 atm.; $0{\cdot}0_3268$, between 1000–1500 atm.; $0{\cdot}0_3167$, between 1500–2000 atm.; $0{\cdot}0_3123$ between 2000–2500 atm.; and $0{\cdot}0_493$ between 2500–3000 atm. Observations were also made by F. M. Penning, A. W. Witkowsky, P. Koch, and M. W. Travers. L. Holborn and J. Otto gave $pv=1{\cdot}73317+0{\cdot}72317p+1{\cdot}8167p^2$ at 200°; $pv=1{\cdot}36713+0{\cdot}20933p+3{\cdot}1000p^2$ at 100°; and $pv=1{\cdot}00080-0{\cdot}79333p+5{\cdot}2222p^2$ at 0°. V. Fischer, W. J. Walker, P. Weiss, and E. Fouché discussed the **equation of state** of nitrogen.

O. E. Meyer[3] and numerous others have measured the **viscosity** of atm. air.

The values at 0° range from $\eta=0{\cdot}0_31679$ to $0{\cdot}0_31880$; at 20° from $\eta=0{\cdot}0_31780$ to $0{\cdot}0_31980$:

	−191·4°	−145°	−115°	−82°	−38°	0°
η . .	$0{\cdot}0_4579$	$0{\cdot}0_4240$	$0{\cdot}0_4590$	$0{\cdot}0_31060$	$0{\cdot}0_31570$	$0{\cdot}0_31880$

The following data for temp. up to 100° are by O. Schumann, for 197·3° by A. von Obermayer, for 302° by P. Breitenbach; and for the remaining temp., by W. J. Fisher:

	0°	40°	80°	100°	197·3°	302·3°	501·2°
η .	$0{\cdot}0_31679$	$0{\cdot}0_31896$	$0{\cdot}0_32153$	$0{\cdot}0_32290$	$0{\cdot}0_32538$	$0{\cdot}0_32993$	$0{\cdot}0_33606$

R. A. Millikan gave for the best representative value at 23°, $\eta=0{\cdot}0001824$; and for temp., $\theta°$, between 12° and 30°, $\eta=0{\cdot}0_318240-0{\cdot}0_6493(23-\theta)$. E. L. Harrington gave 0·00018226 at 23°, and K. S. van Dyke, 0·00018221. Numerous formulæ have been proposed. W. Sutherland gave $\eta=\eta_0 1{\cdot}414145(1+0{\cdot}003665\theta)\frac{1}{2}(1+113T^{-1})-1$; O. E. Meyer, $\eta=\eta_0(1+0{\cdot}003665\theta)0{\cdot}760$; and S. W. Holman found that at $\theta°$, the viscosity $\eta=0{\cdot}00017155(1+0{\cdot}002751\theta-0{\cdot}0000000034\theta^2)$. J. H. Jeans gave $\eta=\eta_0(T/273)^{0{\cdot}76}$. F. A. Williams also studied the effect of temp. on the viscosity of air. L. Gilchrist showed that the presence of unsaturated water vapour in the air has no measurable effect on the viscosity at normal press. and 20°.

Dew-point . .	6·6°	11·6°	14·1°	17°	Saturated
$\eta\times10^7$ . .	1·810	1·816	1·811	1·807	1·816

Although the average value for unsaturated air is about 0·3 per cent. less than for saturated air, G. Zemplén obtained a greater difference, *viz.*, 0·8 per cent., and W. Crookes found that the presence of water vapour did not affect the coeff. of viscosity of air until the total press. was less than half the normal press., and for lower press. the viscosity diminishes, but not so much as is required by formulæ based on the kinetic theory of mixed gases. J. C. Stearns discussed this subject. K. Przibram described a demonstration experiment. S. Ray obtained a negative result for the effect of a transverse electric field on the viscosity of air. F. Kleint measured the viscosities of various mixtures of oxygen and nitrogen gases; and P. Breitenbach, of mixtures of ethylene and air. J. E. Verschaffelt and co-workers measured the viscosity of liquid air and of various mixtures of oxygen and atm. nitrogen, and found at −193·53°, $\eta=0{\cdot}001599$ with 9·5 per cent. oxygen; 0·001678 with 35 per cent. oxygen; 0·001865 with 61 per cent. oxygen; and 0·001895 with 91 per cent. oxygen. S. Chapman and E. A. Milne discussed the rapid increase in the effective kinematical viscosity of air at great heights owing to the decrease in density.

According to L. Grunmach,[4] the **surface tension** of liquid air at −190·3° containing 49·9 vol. per cent. of oxygen is 11·61 dynes per cm.; and the **specific cohesion,** 2·406 sq. mm. and liquid air with 65·3, 67·6, and 76·45 vol. per cent. of oxygen has the respective surface tension 12·05, 11·91, and 12·51 dynes per cm., and for the values of the sp. cohesion, 2·376, 2·312, and 2·376 sq. mm. The **diffusion** coeff. of carbon dioxide and air at 0° was found by J. Loschmidt to be 0·142 sq. cm. per sec., and by K. Waitz, 0·136; A. von Obermayer gave for air and oxygen, 0·178 at 0°; J. Stefan, for air and carbon disulphide, 0·0995 at 0°; F. A. Schulze, for air and hydrogen, 0·661 at 17°; F. Houdaille, air and steam, 0·203 at 0°; and G. Guglielmo, air and steam 0·239 at 8°, and 0·248 at 18°. A. Winkelmann reported observations on this subject. T. Graham measured the rate of diffusion of air through porous plugs. C. Barus discussed the slow diffusion of air in water. J. Dewar found that air, at atm. press. and 15°, diffused through rubber 0·01 mm. thick at the rate of 2·0 c.c. per sq. cm. per day. L. Dufour, and E. Reusch observed that dry air diffuses more rapidly than moist air through a porous septum, and through hydrophane. J. Sameshima and K. Fukaya studied the atmolysis of air. Measurements of the **velocity of sound** in air at 0° range from M. Frot's [5] 330·7 metres per second to G. Moll and A. van Beek's 332·77 metres per second. F. Himstedt and R. Widder found the ratio of the velocities of sound in air at 20° and at —78·73° to be 0·8147. The relation of the velocity to the sp. ht. was discussed by A. Leduc. S. R. Cook observed 216·73 metres per second at —150·0°, and 253·75 metres per second at —106·2°. E. H. Stevens found for the velocity, V, in metres per second:

	0°	100°	300°	500°	750°	1000°
V . .	331·32	386·5	478·1	552·8	632·0	700·3

Observations were also made by H. B. Dixon and co-workers. N. de Kolossowsky studied the relation between the velocity of sound and the speed of translation of the molecules.

Observations on the dimensions of the constituent molecules were made by A. O. Rankine,[6] E. Dorn, W. Sutherland, W. Altberg, C. Ramsauer, and P. Lenard. The mean **velocity** of the molecules, at 0° and 760 mm. press., is given as 44,690 cm. per second; the mean **free path,** $0{\cdot}0_5608$ cm.; and the **molecular diameter,** $0{\cdot}0_731$ cm. K. S. van Dyke, and E. Blankenstein discussed the coeff. of slip, and of momentum transfer in air; and D. Brunt, the kinetic energy of the atmosphere.

E. H. Amagat[7] found the coeff. of **thermal expansion** to be 0·00367 for dry air, and 0·00368 to 0·00369 for moist air; P. von Jolly gave 0·00366957; and D. I. Mendeléeff and N. Kajander, 0·003684 at atm. press. A. Cazin found the coeff. of expansion at 5 atm. to be the same as at 1 atm. press. H. Teudt obtained an abnormally high expansion between 350° and 500°, and attributed the results to mol. dissociation. This, however, has not been confirmed by other workers. A. Jaquerod and F. L. Perrot gave 0·0036643 between 0° and 1066°. According to E. H. Amagat, the value of α at constant press., p atm., at different temp. is:

	0° to 15·7°			0° to 99·4°			99·4° to 200·4°		
p .	200	1000	3000	100	500	1000	200	500	1000
α .	0·00475	0·00206	0·00110	0·00444	0·00331	0·00314	0·00287	0·00241	0·00171

and at constant press., the values of the coeff. β are:

	0° to 15·7°			0° to 99·4°			99·4° to 200·4°		
p .	100	1000	2400	100	300	500	100	200	400
β .	0·00446	0·00567	0·00403	0·00462	0·00600	0·00617	0·00319	0·00351	0·00360

Observations were also made by L. Holborn and H. Schultze; and A. W. Witkowsky found for 0° to 100° at 10 atm. α=0·00375, and from 0° to 16°, 0·00376. At 30 atm. press., at temp. ranging from 0° to θ°:

θ	100°	16°	—78·5°	—130·5°	—140°	—145°
α	0·00392	0·00398	0·00420	0·00434	0·00492	0·00519

and from 0° to 100°, at p atm. press.:

p . .	10	30	50	70	90	110	120
α . . .	0·00375	0·00392	0·00410	0·00425	0·00437	0·00445	0·00449

R. Mewes discussed the deviations from Charles' law.

Measurements of the **thermal conductivity** of air at 0° range from P. A. Eckerlein's[8] 0·00004677 to W. Schwarze's 0·00005690. L. Graetz gave $0{\cdot}0_44838$ at 0° and $0{\cdot}0_45734$ at 100°; A. Schleiermacher's values are $0{\cdot}0_4562$ at 0° and $0{\cdot}0_47197$ at 100°. P. A. Eckerlein gave $0{\cdot}0_43678$ at —59° and $0{\cdot}0_42146$ at —149·5°. Observations were also made by D. J. Janssen, A. Winkelmann, P. Compan, A. Kundt and E. Warburg, E. Müller, and H. Gregory and C. T. Archer, who gave $K=0{\cdot}0000583(1+0{\cdot}000297\theta)$; E. Schneider gave $0{\cdot}0002477(1+0{\cdot}0039\theta)$; and S. Weber, $0{\cdot}0002379(1+0{\cdot}00365\theta)$. H. Gregory and C. T. Archer found that by varying the press. from 760 mm. to 360 mm., the thermal conductivity of air was not changed; but on further decreasing the press., a decrease in conductivity became apparent, but did not amount to more than a few per cent. until the press.

fell below 1 mm., when the conductivity began to fall off rapidly. E. O. Hercus and T. H. Laby studied this subject.

F. de la Roche and J. E. Bérard[9] gave for the **specific heat** of air at constant press. c_p=0·2669 from 0° to 100°; H. V. Regnault, 0·238 between 30° and 10°; 0·237 between 0° and 100°, and 0·237 between 0° and 200°; W. F. G. Swann gave 0·2414 at 20°, and 0·2430 at 100°; and K. Scheel and W. Heuse, 0·2409 at 20°, 0·2433 at −76°, and 0·2500 at −181°; E. Wiedemann, c_p=0·2389; R. Thomas, 0·2345 at 17° to 35°; R. Oehme, 0·2371 at 20°; H. N. Mercer, 0·2403; A. Eggert, 0·2372 at 0°; and W. Escher, 0·2376 at 50°. F. Keutel gave C_v=4·90 for the mol. heat of air at one atm. press., at 0°, and between 0° and 1000°, C_v=4·90+0·000436. R. Thibaut gave C_p=7·075 at 350°; and K. Scheel and W. Heuse, 6·965 at 20°. Observations were also made by F. Kohlrausch, L. Witte, A. Cazin, E. H. Amagat, E. Schreiner, A. Wüllner, V. Fischer, W. D. Wormesley, K. Nesselmann, and A. W. Witkowsky. According to L. Holborn and L. Austin, the effect of raising the temp. is to raise the sp. ht. of air, freed from carbon dioxide, thus:

	0°	100°	200°	400°	600°	800°	1000°	1200°	1400°
c_p .	0·2405	0·2415	0·2424	0·2443	0·2453	0·2481	0·2500	0·2519	0·2538

These results were represented by the formula $c_p=0{\cdot}2405+0{\cdot}0_5 95\theta$. W. D. Womersley gave for the sp. ht. at constant vol., c_p=0·2002 or C_v=5·803 between 0° and 1500°; and c_v=0·2056 or C_v=5·961 between 0° and 2000°. R. T. Glazebrook discussed these results. The observed values in the proximity of room temp. range from C_p=6·796 to 7·755; and C_v=4·801 to 5·742. H. B. Dixon and co-workers gave $C_v=4{\cdot}8+0{\cdot}0004T$. For the effect of press. on the sp. ht. of air at 20°–100°, L. Holborn and M. Jacob gave for p in kgrms. per sq. cm.:

p .	1	25	50	100	150	200	300
c_p .	0·2415	0·2490	0·2550	0·2690	0·2821	0·2925	0·3026
C_p .	6·991	7·209	7·394	7·788	8·167	8·468	8·760

For the ratio of the two sp. hts. at 0°, A. Leduc gave 1·404; E. Grüneisen and E. Merkel, 1·4034; J. R. Partington and co-workers, 1·4103 at 17°; H. N. Mercer, 1·400; W. C. Röntgen, 1·405 at 18°; H. W. Moody, 1·4011 at 20°; K. Schöler, 1·40 at 20° and 1 atm., or 1·41 at 20° and 3 atm. press.; A. Kalähne, 1·39 at 900°; O. Lummer and E. Pringsheim, 1·4025 at 5° to 14°; J. Jamin and F. Richard, 1·41; H. Kayser, 1·412 at 0°; P. A. Müller, 1·4046 at 16°; E. Paquet, 1·4038; J. W. Low, 1·3947; G. Maneuvrir, 1·395; W. Makower, 1·402; B. Hartmann, 1·413 at 12°; M. Guéritot, 1·403; M. C. Shields, 1·4029 at 20°; and T. C. Hebb, 1·4031 at 0°; K. Scheel and W. Heuse, 1·401 at 20°, 1·402 at −76°, and 1·448 at −181°; E. H. Stevens, 1·40 at 0° and 100°, and 1·34 at 950°; and W. Koch, at −79°, 1·40 at one atm. press., 2·20 at 100 atm. press., and 3·33 at 200 atm. press. The observed values in the proximity of room temp. range from 1·347 to 1·415. J. H. Brinkworth gave 1·4032 for the ratio at 17°, and 1·4154 at −118°. G. Piccardi studied the thermal capacity of air.

The **Joule-Thomson effect** for air was measured by J. P. Joule and W. T. Thomson,[10] J. P. Dalton, E. Vogel, F. Nöll, L. G. Hoxon, J. R. Roebuck, K. Olschewsky, F. G. Keyes, H. Hausen, N. Eumorfopoulus and J. Rai, and W. P. Bradley and C. F. Hale. Expressing the press. in kilograms per sq. cm., F. Nöll found the results indicated in Table VIII.

In 1732, H. Boerhaave[11] tried without success to condense air to the liquid state by artificial cold; and in 1850, J. Natterer likewise failed in an attempted **liquefaction** of air, although he compressed the gas under nearly 3000 atm. press.; but in 1877, L. Cailletet obtained liquid air in the form of a mist by compressing dried air, freed from carbon dioxide, at the temp. of liquid nitrous oxide, and under 200–225 atm. press., and suddenly releasing the press.; and in 1884, J. Dewar described a method of liquefying air cooled by means of liquid or solid nitrous oxide —*vide* 1. 13, 25. Various forms of apparatus have been devised for liquefying air

TABLE VIII.—JOULE-THOMSON EFFECT AT DIFFERENT TEMPERATURES AND PRESSURES.

Temp.	Pressure.				
	0	25	50	100	150
−55° . . .	0·44	0·40	0·37	0·28	0·18
−34° . . .	0·38	0·34	0·31	0·24	0·17
−0·6° . . .	0·27	0·25	0·24	0·19	0·16
49° . . .	0·20	0·18	0·17	0·15	0·12
100° . . .	0·14	0·13	0·13	0·10	0·08
150° . . .	0·09	0·09	0·07	0·06	0·05
199° . . .	0·05	0·04	0·04	0·04	0·03
250° . . .	0·02	0·02	0·02	0·01	0·01

and preserving the liquid, by J. Dewar, C. von Linde, K. Olschewsky, A. Stock and B. Hoffmann, R. Pictet, R. Mewes, G. Claude, F. G. Cottrell, W. P. Bradley and G. O. P. Fenwick, etc. Probably, L. Cailletet first solidified air in 1878; and in 1894, J. Dewar obtained it as a clear, transparent solid. The equilibrium relations in the liquefaction of air were studied by J. H. Simons.

For the **critical temperature** of air, K. Olschewsky[12] gave —140·0°, and for the **critical pressure,** 39·0 atm.; S. von Wroblewsky gave respectively —141·0° and 39·2 atm.; A. W. Witkowsky, 140·9°, and 39 atm.; and E. H. Amagat, —140·7° and 35·9 atm. The last-named gave 0·344 for the **critical density.** J. P. Kuenen and A. L. Clark gave for the critical temp., —140·63° to —140·53°; for the critical press., 37·17 to 37·27 atm.; and for the critical density, 0·31 to 0·35. S. F. Pickering gave for the best representative values T_c=132·4° K.; p_c=37·2 atm.; and D_c =0·33 grm. per c.c. S. von Wroblewsky gave —192·2° for the **boiling point** of liquid air, and K. Olschewsky, —191·4°. The latter also measured the **vapour pressure,** p atm., of liquid air at different temp. with the following results:

	−205°	−191·4°	−176°	−169°	160·5°	−152°	−146°	−142°	−140°
p . .	0	1	4·0	6·8	12·5	20·0	27·5	33·0	39·0

S. von Wroblewsky said that while in many of its properties atm. air behaves like a homogeneous gas, so that its critical constants have been determined, yet the liquefaction of air is accompanied by various complex phenomena, resembling those noticed in the compression of a mixture of five volumes of carbon dioxide with one of air. Thus, if atm. air is compressed until the meniscus first formed disappears, and the press. allowed to decrease slowly, there are produced two superposed menisci, separating heterogeneous fluids, in which the relative proportion of oxygen and nitrogen is different, the lower fluid containing about 21·3 per cent., and the upper 17·5–18·5 per cent. oxygen. Secondly, the vap. press. curves of atm. air are not regular, inasmuch as on compression the temp. at first sinks uniformly in proportion to decrease of press., until a minimum point at —198° is reached; on further compression the temp. begins to rise to a maximum at —196°, and thence decreases. These irregularities of the vap. press. curves show that the two constituents of the air are not vaporized equally, and the temp. observed is dependent on the momentary composition of the fluid. J. P. Kuenen and A. L. Clark studied the condensation phenomena in the critical region; they found the temp. and press. corresponding with the plait-point are —140·73° and 37·25 atm., and with the critical point of contact, —140·63° and 37·17 atm. The density of the liquid at these points is 0·35 and 0·31. The critical density of air calculated from the critical densities of oxygen and nitrogen by the simple mixture rule is 0·34.

The composition of liquid air in equilibrium with its vapour has been determined by E. C. C. Baly—*vide* Figs. 25 and 26, **1.** 13, 26. His values for absolute temp. of the boiling liquid and vapour with different mol. percentages of oxygen are:

O_2	0	10	20	40	60	80	90	100 mol. per cent.
$T_{\text{vap.}}$	77·54°	79·6°	81·3°	84·4°	87·0°	89·1°	90·0°	90·96°
$T_{\text{liq.}}$	77·54°	78·3°	78·8°	80·7°	83·1°	86·3°	88·4°	90·96°

J. K. H. Inglis determined the compositions of liquid and vapour in equilibrium with each other during the isothermal distillation of mixtures of liquid oxygen and nitrogen at $-74{\cdot}7°$, $-198{\cdot}3°$ and $-193{\cdot}93°$. If R_v and R_l are the respective ratios of nitrogen to oxygen in vapour and liquid, and m, the molar percentage of nitrogen in the liquid, then, at $-198{\cdot}3°$, $R_v/R_l=5{\cdot}48-0{\cdot}0207m$. When the total and partial press. of the oxygen and nitrogen are plotted, the curves have only a slight curvature. The results also show that the solubility of nitrogen in oxygen is in accord with Henry's law (**1.** 10, 4) up to a molar percentage of 70; after that, the variation of the quotient C/p for oxygen indicates an association of the oxygen mols. dissolved in the liquid nitrogen. The phenomena connected with the isothermal distillation or fractional condensation of liquid air have been discussed by A. Grusinoff, G. Claude, H. Erdmann, D. A. Goldhammer, K. T. Fischer and H. Alt, E. A. le Sueur, J. K. H. Inglis and J. E. Coates.

The **heat of evaporation** of liquid air was measured by T. Estreicher,[13] and U. Behn. According to J. S. Shearer, the heat of vaporization depends on the proportion of oxygen; and G. Witt represented the latent heat of vaporization of liquid air by $L=49{\cdot}59+0{\cdot}0143p$ cals., where p represents the percentage of oxygen in the mixture; the latent heat of vaporization of nitrogen is 49·59 cals., and of oxygen, 51·92.

Numerous observations [14] have been made on the **index of refraction** of dry atm. air for the D-line, and numbers ranging from $1{\cdot}0_32911$ of L. Lorenz to $1{\cdot}0_32947$ of E. Ketteler have been reported. H. Kayser and C. Runge gave the following data where the values of μ should have 1·000 . . . prefixed to them:

λ	0·759	0·687	0·656	0·589	0·527	0·486	0·431	0·397	0·393
μ	2905	2911	2914	2922	2933	2943	2962	2978	2980

λ	0·382	0·373	0·359	0·344	0·336	0·329	0·318	0·310	0·302	0
μ	2987	2993	3003	3015	3023	3031	3043	3053	3064	3

E. W. Cheney found $1{\cdot}0_32925$ for $\lambda=5852$ A.; $1{\cdot}0_32919$ for $\lambda=6143$ A.; and $1{\cdot}0_32912$ for $\lambda=6678$ A. A. Pérard found for the visible spectrum:

λ	0·4358	0·5461	0·5780	0·5986	0·6438μ
μ	$1{\cdot}0_329668$	$1{\cdot}0_329334$	$1{\cdot}0_329273$	$1{\cdot}0_329421$	$1{\cdot}0_329177$

The index of refraction is proportional to the press. at 600 mm. and 760 mm.; and it is related to temp., θ, by $\mu_0-1=(\mu-1)(\times 0{\cdot}003716\theta)$, where μ_0 is the index of refraction at 0°, and μ that at $\theta°$. V. Posejpal, and A. Mallock made some observations on the effect of press., p, on the sp. refraction of air, and found $\mu-1=0{\cdot}36269\times10^{-6}p(1+0{\cdot}0_5357p)$. W. Traub represented his results between $\lambda=0{\cdot}185\mu$ and $0{\cdot}546\mu$ by $(\mu-1)10^7=551716/(199{\cdot}5534-\lambda^{-2})-4880{\cdot}3/(43{\cdot}8193-\lambda^{-2})$; J. Koch gave $(\mu^2-1)10^8=57642+327{\cdot}7/(\lambda^2-0{\cdot}005685)$; and L. Lorenz, $\mu=\mu_0-0{\cdot}0_155f/(1+a\theta)$, when μ_0 represents the index of refraction of dry air at the same temp. and press., and f mm. denotes the partial press. of the mixture in the atmosphere; M. Opladen studied the effects of between 1 and 10 atm. press. G. D. Liveing and J. Dewar gave $\mu=1{\cdot}2062$ for the index of refraction of liquid air for the D-line. A. Zwetsch studied the effect of press. on the index of refraction of air. E. Stoll gave for the **dispersion of light** for $\lambda=4388$ to 9224 A., in air, $(\mu-1)10^7=2871{\cdot}87+16{\cdot}170\lambda^{-2}$, where λ is expressed in μ. Lord Rayleigh, and J. Cabannes and J. Granier studied the polarization and the scattering of light in air. G. I. Pokrowsky, and D. Banerji concluded that the scattering of light in the atmosphere is largely due to small particles of dust.

There are numerous phenomena produced in the atm. by foreign substances in suspension—*vide infra.* The subject is discussed by J. M. Pernter and F. M. Exner in their *Meteorologische Optik* (Berlin, 559, 1910), and W. J. Humphrey in his

Physics of the Air (Philadelphia, 426, 1920). The apparent magnification of the zenith distance of celestial objects is produced by the so-called astronomical refraction discussed by Lord Rayleigh,[15] A. R. McLeod, and others; the twinkling of stars was examined by L. Respighi. The **refraction of light** by a mass of water droplets suspended in air produces rainbows, etc.; the refraction of light by minute ice crystals of the cirrus and other clouds produces haloes of various kinds; the **diffraction of light** from cloud droplets produces commas, iridescent clouds, and the mountain-spectre or Brocken-spectre; and the scattering of light by the molecules of air produces the blue colour of the sky. The **polarization** of sky-light, discovered in 1811 by D. F. J. Arago, is produced by reflection from relatively large particles—cloud droplets, dust, etc.—and the combination of primarily and secondarily scattered radiation. This subject was discussed by Lord Rayleigh, C. Soret, etc. The **electromagnetic rotation of the plane of polarization,** ω, for light of wave-length, λ, between $0{\cdot}423\mu$ and $0{\cdot}684\mu$, at 13°, was represented by L. H. Siertsema[16] by $\omega = 0{\cdot}0001915\lambda^{-1} + 0{\cdot}00004619\lambda^{-3}$.

The **colour** of a cloudless sky is generally blue, but, according to circumstances, it may have the whole range of spectral tints. The zenith at great altitudes is distinctly violet, and at moderate altitudes blue; as the angular distance from the vertical increases the colour finally merges into a grey near the horizon. Just after sunset, or before sunrise, different parts of the sky may appear green, yellow, orange, or dark red, dependent on the humidity and dust content of the atmosphere. Attempts to explain the blue colour date from the sixteenth century, when Leonardo da Vinci suggested that the blue is a mixture of white light with that of black space. Isaac Newton[17] attributed the blue colour to a kind of interference between the rays reflected from the front and rear surfaces of minute transparent drops of water. R. Clausius showed that such droplets would cause the stars and celestial objects to appear much magnified; and he assumed that the droplets must be hollow. E. Brücke showed that the droplets are not hollow, and that the blue produced by the droplets of water is not the same as the blue of the sky. He further showed that a transparent medium containing a sufficient number of small particles appears blue when illuminated with white light; and that objects can be seen clearly and distinctly through such a medium. J. Tyndall demonstrated that such particles with incident white light, scatter blue light which is completely polarized at right angles to the incident beam. Lord Rayleigh proved that in the absence of all dust the light scattered by the molecules of air are sufficient to give a blue sky; and, added L. V. King, molecular scattering is sufficient to account completely for both the attenuation of solar radiation, and the intensity and quality of sky radiation. W. Spring considered the blueness of the sky to be due to the blue colour of the contained oxygen, ozone, and water vapour, since the rays which reach the eye, after reflection, and possibly after multiple reflections, will have traversed a longer path in the absorbing medium than the direct rays of the sun. It has just been shown, however, that the colour of the sky would be blue quite apart from selective absorption by oxygen or of its compounds. A bibliography on this subject has been compiled by N. E. Dorsey.

The **spark spectrum** of air is complex and is formed by the superposition of the spectra of its components. The relative intensities of some of the lines are altered by the partnership. A. J. Angström[18] found the spectrum showed mostly the lines of nitrogen, and it was quantitatively examined by D. Alter, A. Masson, and V. S. M. van der Willigen. The lines were measured by G. Kirchoff, W. A. Miller, W. Huggins, F. Exner and E. Haschek, P. W. Merrill and co-workers, A. Hagenbach and H. Konen, J. M. Eder and E. Valenta, F. Brasack, R. Thalén, L. de Boisbaudran, etc. J. Formanek gave for the more important lines in the spectrum of air 6563 in the red; 5943 and 5933 in the orange-yellow; 5711 and 5679 in the yellowish-green; 5535, 5496, 5454, 5177, 5046, 5006, 5003, and 4941 in the green; 4804, 4789, 4707, 4648, 4642, 4633, and 4606 in the blue; 4447, 4432, 4416, 4414, 4348, 4319, and 4241 in the indigo; and 4237, 4200, 4137, 4093, 4069, and 3995 in the violet. The effect of *pressure* was examined by L. Cailletet, A. Cazin, etc., who found the lines broadened with increasing press. A. Wüllner, and E. Goldstein examined the **band spectrum** of air. W. N. Hartley and W. E. Adeney, G. G. Stokes, J. Trowbridge and C. C. Hutchins, L. Ciechowsky, O. Neovius, J. J. Hopfield, and E. B. Frost and W. S. Adams examined the **ultra-violet spectrum** ; W. Schwetz, the **ultra-red spectrum** ; and J. Dufay, the spectrum of lightning.

The *aurora polaris*, or *aurora borealis*, or *aurora australis*, or *zodiacal light* is an imperfectly-understood luminous phenomenon of the upper atmosphere. It appears in various forms, being sometimes quiescent, and at others very changeable, showing arcs, bands, rays, curtains, patches, diffuse glows, and coronas. The colour is usually white, sometimes it is variegated red, yellow, or green. A great many observations have been made on the spectra of the different forms of the zodiacal light by J. R. Capron, H. Kayser, S. Arrhenius, etc. Much of the light is due to nitrogen bands, but the source of a green line $\lambda = 0.5577$ is not known. It has been attributed to krypton, but other krypton lines are absent, and it is considered very doubtful if sufficient krypton is present to produce so intense a line. The brilliant shifting auroral displays are usually accompanied by magnetic storms, and they are more numerous during years of sun-spot maxima than during years of sun-spot minima. It has been suggested that the aurora is produced by negative particles shot from the sun and entrapped by the magnetic field of the earth ; but L. Vegard and C. Störmer suggested that the phenomenon is produced by streams of positively charged α-particles in the upper atmosphere shot off by radioactive substances in the sun. They added that the green auroral line is due to the phosphorescence of solid nitrogen under the electronic bombardment, but J. C. McLennan could not verify this. The only line observed when solid nitrogen is bombarded by cathode rays is $\lambda = 5231$ A. J. C. McLennan, H. J. C. Ireton and K. Thompson, G. Caris, and D. A. Keys showed that the line is primarily due to oxygen, no oxygen, no 5577-line. Lord Rayleigh showed that the non-auroral light has its green line 5577 A., without the negative band spectrum of nitrogen, and it is suggested that it may be a phenomenon of phosphorescence excited by the sun in the day-time, and carried round by the earth's rotation.

G. D. Liveing and J. Dewar examined the **absorption spectrum** of liquid air. H. Buff reported that dry air absorbs 50 to 60 per cent. of the heat rays from a source at about 100°, and that the absorptive power of dry air exceeds that of moist air. J. Tyndall, on the contrary, found air to be quite diathermous. N. Egoroff examined the absorption of sunlight by the atm., and H. Wild showed that if dust be excluded, dry or moist air absorbs very little light.

C. G. Abbot and F. E. Fowle [19] estimate that of the total radiant energy delivered from the sun to the earth, about one-third—37 per cent.—is dissipated, for it is scattered into space by clouds, dust particles, or air molecules, and reflected from the surface of the earth. Of the remaining 63 per cent., about half is directly absorbed by the earth, and half by the atmosphere. In addition to the absorption or Fraunhofer lines inherent in the solar spectrum, there are many deficiencies resulting from the passage of solar energy through the earth's atm., and caused mainly by oxygen, ozone, carbon dioxide, and water vap. The three last named strongly absorb the long wave-length radiation from the earth. According to E. L. Nichols, the selective absorption of sunlight by the atm. is very marked. At 0.8μ, just beyond the visible red spectrum, about 8 per cent. of the sun's rays are cut off, while in the violet, at least half the light is absorbed ; it is for this reason too that the spectrum of solar light ends soon after the boundary of the visible spectrum is reached, and why many rays present in the spectra of artificial sources of light are absent from the solar spectrum. The eye is most sensitive to those rays which in the spectrum of sunlight are of maximum energy. Sunlight which has not been filtered through the atm. contains so much more ultra-violet radiation that it is necessary to protect the eyes by coloured glass at high altitudes. This is not only because of the excess glare above the snow line, but also because of the dangerous ultra-violet rays. Nitrogen and argon have no known absorption bands, and oxygen has only one band, and that is in the extreme ultra-violet or Schumann region. The absorption of light by air was examined by A. Kreusler, and E. Warburg. The reflecting power of the earth is small, and the atm. is nearly opaque to terrestrial radiations, and it is estimated that approximately 60 per cent. of the incident solar energy ultimately heats the earth's atm.

Bolometric observations show large water vapour absorption bands, and it is therefore inferred that most of the solar energy directly absorbed by the atm. is due to the water vap. All these absorption bands are of longer wave-length than the region of maximum intensity in the solar spectrum, so also are the absorption bands of carbon dioxide and ozone. The amount of solar energy absorbed by oxygen, nitrogen, and argon is negligibly small in comparison with the absorption due to water vap., ozone, and carbon dioxide. The absorption of terrestrial radiation by water vap., ozone, and carbon dioxide is indicated in Fig. 2, by C. G. Abbot and F. E. Fowle. The thick curve represents the energy distribution of radiation from a black body at 287·2° K. The area of this curve below the irregular full line near the top extending as far at least as 20μ shows the absorption of the earth's radiation by a column of 1·13 grms. of water vap. per sq. cm. cross-section as computed by H. Rubens and E. Aschkinass; this amount of water vap. was computed by C. G. Abbot and F. E. Fowle to be the average amount in the atm. as a whole above the 1780 metre level. The areas below the two broken curves show the absorption by carbon dioxide above the same level as computed by H. Rubens and E. Aschkinass, and C. Schäffer. The area below the dotted curve represents the absorption of the earth's radiation estimated from E. Ladenburg and E. Lehmann's observations. The absorption of the solar radiations by ozone plays an important part in the life of animals and plants. Thus, B. Moore said:

> As the light from the sun first strikes the earth's atm., perhaps one or two hundred miles above, it is full of ultra-violet light, and violet light. Such light rays as these, if they reached the earth at the present moment, would annihilate us; they would simply mean death to the world below. The first thing that happens to prevent this is that ozone is developed, and by absorption this ultra-violet light is shut out. The solar spectrum of sunlight is known to be marked out, to be limited, by the ozone developed in the upper atm., and it has been shown that if there were only a millimetre of ozone interposed between quartz plates nearly all this light, which is germicidal light, would be shut out. It is not completely shut out as the light passes through the air, and that is why there must be natural colour screens in plants and animals and man.

P. Lenard[20] showed that in addition to the **photoelectric effect** produced on a charged metallic surface struck by ultra-violet rays, there is a volume effect which takes place in the gas about the metal. The ionization is produced by the absorption of the ultra-violet rays by the gas itself. The effect with air was further studied by A. L. Hughes, T. Lyman, D. H. Loughridge, and F. Palmer. J. A. McClelland and J. J. M'Henry studied the nuclei produced in moist air by ultra-violet light; H. Kulenkampff, the ionization of air by X-rays and cathode rays. The **absorption of X-rays** from cathodes of different metals by air was studied by R. Whiddington, P. W. Burbidge, and G. Owen; the **scattering of X-rays** in air, by C. G. Barkla, C. G. Barkla and C. A. Sadler, and J. A. Crowther; the absorption of radiations emitted by a high resistance when traversed by an electric current, by G. Reboul; the mobilities of the ions in air, by M. Laporte; W. Kliefoth, the electrostriction effect; and A. H. Taylor and E. O. Hulburt, the absorption of radio-waves in the upper atmosphere.

The earth is not electrically neutral, for its surface is coated with a charge of negative electricity which gives rise to a positively charged electric field in the atm. Near the beginning of the eighteenth century, F. Hauksbee,[21] J. Wall, and S. Gray compared the discharge of electricity from a charged vessel across air to thunder and lightning; and in 1749, B. Franklin showed that "clouds that contain lightning are electrified." G. Beccaria made observations on atm. electricity extending over a number of years. L. G. le Monnier showed that tall insulated conductors become electrified when exposed to air with a clear sky; and C. A. Coulomb, and W. Linss found that the most perfectly insulated conductors lose their charges when exposed to air. These facts depend on the **electrical conductivity** of atm. air. The electrical state of the atm. produces the spectacular displays of lightning in thunderstorms, the aurora polaris, and St. Elmo's fire (*i.e.* a branch discharge from elevated objects).

According to L. A. Bauer and W. F. G. Swann, when the potential gradient at the surface of the earth is 100 volts per metre, the charge is 2·65 negative electrostatic units per sq. cm., or $4{\cdot}5\times10^5$ coulombs for the whole surface; and the net charge of the air is roughly 0·1 electrostatic unit of positive electricity per cubic metre. The **potential gradient** or the change of potential in rising one metre from the earth's surface is about 150 volts; it is rather less for the second metre, less again for the third, until about 10 kilometres high, it is practically zero. The potential gradient varies with location, being smaller in valleys than on the neighbouring ridges; it is generally smaller in tropical regions than in temperate climes; and it is larger in winter than in summer. The potential gradient is a minimum about 4 a.m., and may rise to a maximum about 9 a.m., and fall to a second minimum about 2 p.m., rising to a second maximum about 10 p.m., or there may be only one maximum at 2 to 4 p.m. Wind, smoke, dust, fog, rain, etc., modify and even reverse the normal potential gradient. C. Ramsauer also measured the decrease of potential vertically upwards from the earth.

L. A. Bauer and W. F. G. Swann gave $1{\cdot}44\times10^{-4}$ for the positive ion conductivity of air over land during clear weather, and for the negative ion conductivity, $1{\cdot}19\times10^{-4}$. The electrical conductivity of the atmosphere is thus extremely small if referred to that of copper as a standard. W. F. G. Swann estimated that a column of air one inch long offers as much resistance to the passage of the electric current as a copper cable 3×10^{16} miles long and of the same sectional area. Such a cable could be wrapped round the earth 8×10^{11} times, and would stretch from here to Arcturus and back about 20 times. The conductivity is generally greater during summer than during winter; and usually high in the morning and low in the evening; it is small when the air is dusty or foggy, and relatively high when the air is clear and dry. The conductivity varies irregularly during the first kilometre elevation, but above that level it increases rapidly, and at 6 kilometres elevation it has 20 times its surface value. According to W. J. Humphreys, the sporadic electric currents, produced in the atm. by lightning discharges, may amount to many thousand ampères; and those due to falling rain, snow, hail, etc. average 10^{-16} amp. per sq. cm. in ordinary rain, but with rain accompanied by thunderstorms, as much as 10^{-2} amp. per sq. cm. has been reported. There are also two forms of electric currents which are always flowing. One is produced by the mechanical or convective transfer of ions from one place to another by winds, etc. The average amounts to 10^{-16} amp. per sq. cm. with the wind passing at a metre per second. The other is due to the downward flow of one kind of ions—generally positive—and the upward flow of ions of the opposite kinds. The average conductive current produced in this way amounts to 3×10^{-16} amp. per sq. cm. R. A. Millikan and I. S. Bowen investigated the conductivity of air at altitudes from 5 to 15·5 kms. The subject was discussed by V. F. Hess, *Die elektrische Leitfähigkeit der Atmosphäre und ihre Ursachen* (Braunschweig, 1926); E. Mathias, *Traité d'électricité atmosphérique et tellurique* (Paris, 1924); and by B. Chauveau, *Électricité atmosphérique* (Paris, 1922). T. A. McLaughlin studied the **cataphoresis** of air-bubbles in various liquids.

According to modern theories, the conductivity of atm. air is produced by ions. C. T. R. Wilson, and H. Geitel discovered that spontaneous **ionization** occurs in the atm.; and E. Rutherford and H. L. Cooke, and J. C. McLennan and E. F. Burton showed that the lower atm. has penetrating rays presumably derived from radioactive substances near the surface of the earth. A. Gockel attributed the ionization of the atmosphere to the influence of the sun as shown by the diurnal and annual variations in the conductivity. P. Langevin also found the existence of large ions of molecular size moving with a comparatively small velocity. These ions are probably the charged nuclei of cloudy condensation discussed by J. Aitken, J. W. Broxon, H. Kulenkampff, G. A. Anslow, W. W. Merrymon, V. I. Baranoff,

J. J. Nolan, J. J. Nolan and J. Enwright, E. Marsden, W. Kohlörster, A. D. Power, J. F. Lehmann and T. H. Osgood, J. Clay, H. A. Erickson, F. Behounek, M. Akiyama, R. A. Millikan and R. M. Otis, F. Ramon y Ferrando, A. Wigand, L. B. Loeb, A. Stäger, A. L. McAulay and N. L. Hutchinson, K. M. Downey, A. Steichen, W. F. G. Swann, A. Pannekoek, R. Glocker and L. M. Valasek. R. A. Millikan and G. H. Cameron, and G. M. B. Dobson studied the ionization of air.

J. Elster and H. Geitel found that a bare wire exposed to air and negatively charged gradually acquires a coating of radioactive material, and H. A. Bumstead found that the radioactive material of the atm. consists essentially of radium and thorium emanations. L. A. Bauer and W. F. G. Swann estimate that the **radioactivity** of air over the Pacific Ocean is eq. to $3{\cdot}3\times10^{-12}$ curie of radioactive emanation per cubic metre; over the Subantarctic Ocean, $0{\cdot}4\times10^{-12}$ curie; and over the land, an average of 88×10^{-12} curie. From E. Rutherford's estimate of the vol. of curie of emanation, the respective vols. of emanation are $1{\cdot}95\times10^{-19}$, $0{\cdot}24\times10^{-19}$ and $51{\cdot}9\times10^{-19}$ part of the atmosphere. These amounts do not suffice to maintain the ionization of atm. air over the oceans, and probably only a part of that over the land—*vide* **4.** 26, 3. It has been estimated that 2 to 6 pairs of positive and negative ions are produced in each c.c. of atm. air per sec. The conc. of the ions does not increase indefinitely because when the conc. reaches 2400 of each kind per c.c. the rate of combination of the ions to form neutral molecules is equal to the rate at which the ions are formed. According to A. S. Eve's estimate, the radioactive material in the earth can account for the production of 4·35 ions per c.c.

	+ ions per c.c.	− ions per c.c.
Mean of land observations	737	668
Mean of sea observations	770	632

E. Rutherford and H. L. Cooke, and J. C. McLennan and E. F. Burton found that air freed from radioactive air and confined in a hermetically sealed vessel, over land, spontaneously forms about 10 ions per c.c. per sec. This is due to the penetrative γ-radiations derived from the radium and thorium, and their disintegration products in the soil. Over the sea, where there is practically no radioactive material, the ions are formed at the rate of 4 ions per c.c. per sec. in a copper or zinc vessel. W. Kolhörster found that with increase of altitude, the ionization within the closed vessel decreases up to an altitude of about 700 metres, showing that the conductivity of the air is produced by the γ-radiations from the radioactive matters in the earth. Above 700 metres, however, the speed of ionization increases rapidly with increasing altitude, until, at 9000 metres, the ions are produced at the rate of 80 per c.c. per sec., and probably higher values at higher altitudes. This suggests a radiation from a source external to the globe or from some agency in the upper regions of the atm. F. Linke says that a layer of strongly radioactive cosmical dust is present in the atm. at an altitude of 20 kms. The ionization of air over the ocean and land is probably due to this cause; while the additional ionization over the land is derived from the radioactivity of the soil—*vide* **4.** 26, 3. S. Chapman and E. A. Milne showed that if the α-particles, at the outer fringes of the atmosphere, possess velocities of the same order as those observed with radioactive substances, if directly incident from outside, the fastest could penetrate to a height of 80 kms. and the slowest 85 kms., and this is independent of the level at which diffusive separation is supposed to commence, and of the presence or absence of hydrogen. This result is to be contrasted with that of L. Vegard, who found that the height reached would be 200 kms. for α-particles with the initial velocity of those from radium-C. The importance of these results is in their bearing on the theory of auroras (which are confined to the 100 kms. to 130 kms. layer); it assumes that they are the manifestation of the absorption by the atm. of α-particles emitted by the sun. The penetration of the atmosphere by β-rays and γ-rays would give rise to well-marked layers of maximum ionization at about 54 kms. and 26 kms. respectively. G. Hoffmann said that there is nothing mysterious about the penetrating radiations at sea-level, for they are derived from known radioactive elements. The origin of the high frequency radiation was discussed by V. F. Hess, R. A. Millikan, F. Behounek, W. Kolhörster, E. Rutherford, W. F. G. Swann, etc. A. Wigand believed that the penetrating radiation of the higher atmosphere has a wave-length shorter than the γ-rays. The radioactivity of air was also studied by W. Schmidt, R. A. Millikan and G. H. Cameron, and L. N. Bogoiavlensky and A. A. Lomakin.

The earth is continually losing negative electricity owing to its potential gradient in a conducting atmosphere. The current from a sq. cm. of the earth's surface is about 2×10^{-16} amp., and from the whole earth, about 1000 amps., and this supply maintains 90 per cent. of the earth's charge which would disappear in 10 minutes if not replenished. If the negative charge of the earth's surface can be explained, there is no need to account for the positive charge of the atmosphere. The conductivity of the atm. increases with altitude, and at 9 kms. its atm. has thirty times the conductivity it possesses at the earth's surface. Hence, with a constant potential gradient, more negative electricity would be driven onward than would be driven from the earth into the atmosphere. Hence, the shell of air below 9 kms. would become positively charged, and the potential gradient would be accordingly reduced. This process would continue until the decrease of the potential gradient with altitude just compensated for the increased conductivity. G. C. Simpson suggested the earth's charge is maintained by the emission of positive and negative corpuscles of a high penetrative power of the sun; the penetration power of the negative corpuscles is greater than that of the positive ones, and sufficient to enable them to reach the earth's surface charging it negatively; while the positive corpuscles are caught by the atmosphere charging it positively. C. T. R. Wilson suggested the ions in the atm. act as nuclei for the condensation of water; and since water condenses more readily on negative than on positive ions, the rain should be charged negatively, the atmosphere positively. As a matter of fact, rain is sometimes charged positively and sometimes negatively—but 75 per cent. of the charge is positive, *i.e.*, of a sign opposite to that required by theory. H. Ebert, and J. Elster and H. Geitel noted that the negative ions of the atm. diffuse more rapidly than the positive ions, so that, with the barometer falling, the highly ionized air in the ground, by a kind of atmolysis, emerges with a positive charge. G. C. Simpson, W. F. G. Swann, and H. Gerdein have shown that this hypothesis is quite inadequate. W. H. Bragg observed that when the γ-rays ionize a gas, the electrons emitted are shot off in the direction of the incident γ-ray. The more penetrating the radiation the greater the effect. Hence, argued W. F. G. Swann, when the penetrating γ-radiations ionize air from above downwards, most of the negative electrons which are emitted will be travelling downwards before they come to rest. Hence, the earth's surface, receiving the negative electrons, will acquire a negative charge, and the atmosphere a positive charge.

H. Ebert, and G. Hoffmann found that liquid air is a non-conductor of electricity, but if pieces of metal be placed therein, an electric charge is acquired. The liquid loses this property if filtered, but acquires it again when exposed to the atm. Water is absorbed, and the friction of the contained ice gives the metal a negative charge while the ice requires a positive charge. The residual ionization of air was measured by W. W. Merrymon. The nature of the ions in air was discussed by H. A. Erikson; and the mobilities of ions in mixtures of air and ammonia, by L. B. Loeb and M. F. Ashley.[22] J. Chadwick and K. G. Emeléus, I. Curie, and L. Meitner and K. Freitag studied the tracks of the α-particles in air. The ionization of air by oxidation processes has been discussed by W. P. Jorissen and W. E. Ringer, and by R. Schenck and co-workers—*vide* **4.** 26, 1. The mobilities of ions in air was discussed by J. J. Nolan, H. A. Erikson, and W. B. Haines; the consumption of energy in the ionization of air, by L. Grebe, and L. Frebe and L. Kriegesmann; the attachment of electrons to the molecules of air, by V. A. Bailey; the transformation period of the positive ions, by L. M. Valasek; the loss of energy of the α-particles in air, by P. L. Kapitza; the ionization of air by electrons, and α-rays, by L. Grebe, T. R. Wilkins, J. F. Lehmann and T. H. Osgood, and G. A. Anslow; the production of β-rays in air by X-rays of short wave-length, by H. Ikeuti. For the **velocity of the ions** in an electric field with a potential difference of one volt per cm., J. Franck gave, for positive ions in dry air at about 15°, and 760 mm. press., 1·35 cms. per second, G. Rothgiesser, 1·331 cms. per second. For negative ions, J. Franck gave 1·82, and G. Rothgiesser, 1·927 cms. per second. With moist air, at 15°, the latter gave 1·325 cms. per second for positive ions and 1·610 cms. per second for negative ions. The **speed of electrons** in air was measured by A. Becker, P. Lenard, A. M. Tyndall and G. C. Grindley, L. B. Loeb, W. Busse, H. B. Wahlin, H. R. Hasse, and J. Robinson. For the **diffusion coefficient of ions** in moist air, J. Townsend gave 0·032 sq. cm. per second for positive ions and 0·035 sq. cm. per second for negative ions; and in dry air, he obtained 0·028 sq. cm. per second with positive ions and 0·043 sq. cm. per second for negative ions. E. Rutherford, J. Franck and W. Westphal, and E. Salles obtained similar data. The **rate of recombination of ions**, $dn/dt = an^2$, where n denotes the conc. of the ions, represented by the ratio a/e, when e denotes the elementary charge in electrostatic units, values ranging from 3200 to 3500—mean, 3368—have been obtained by J. Townsend, R. K. McClung, P. Langevin, L. Hendren, H. A. Erikson, H. Thirkill, H. Ogden, and H. Seeman. W. Busse discussed the monomolecular ions in air; and L. M. Valasek found the rate of change from that of newly formed positive ions with a velocity of 1·87 cm. per sec. to ions with a velocity of 1·37 cm. per sec.

The resistance of the air to the passage of a spark was examined by A. Overbeck,[23] T. Holmen, Lord Kelvin, A. Heydweiller, E. Hospitalier, C. P. Steinmetz, E. Jona, etc. The **discharge tension** of the current required for spherical electrodes at different distances apart in air at different press. has been the subject of many investigations. A. Orgler found with air at different press., p, and with 0·1 and 0·5 cm. spark gaps, the tension required for the discharge was:

p . . .	750	650	450	250	100	60	20 mm.
Kilovolts (0·5) .	17·450	15·470	11·420	7·116	3·579	2·505	1·266
Kilovolts (0·1) .	4·566	4·062	3·120	2·040	1·092	0·795	—

The structure and form of the sparks were studied by T. Terada and U. Nakaya; the point discharge, by J. Zeleny, and W. C. Röntgen; the discharge with cylindrical electrodes, by J. B. Whitehead and co-workers, S. P. Farwell, E. A. Watson, J. W. Broxon, and F. Schaffers; the corona discharge in air, by C. H. Wills; the glow discharge, by W. Stephenson; and the electrodeless discharge, by E. Bouty, and H. Wagner. The potential difference of the cathode for the glow discharge with electrodes of different metals in air was measured by K. Rottgardt,[24] A. Schaufelberger, E. Warburg, and C. A. Skinner. E. Meyer studied the effect of traces of impurities; H. Stücklen, the effect of moisture on the sparking potential of air; and F. Gross, the cathodic spluttering. F. Fernie studied the electrical break-down of air; A. Günther-Schulze, and K. G. Emeléus, the distribution of potential in the glow discharge in air; E. F. Burton, the spark potential; and H. Fischer, the discharge with Tesla currents. J. Estalelle, A. Plante, L. Schopenhauer, and E. Mathias discussed the effect of lightning on atm. air.

The **dielectric constant** of atm. air was found by L. Boltzmann[25] to be 1·000590 at 1 atm. press. and 0°; K. Tangl gave 1·01080 at 19° and 20 atm.; 1·03281 at 60 atm.; and 1·05494 at 100 atm. press.; H. Riegger, 0·001902 at −185·5°; A. P. Carman and K. H. Hubbard, 1·000594 at 0° and 760 mm.; and E. C. Fritts, 1·000540. For liquid air at the b.p. and atm. press., M. von Pirani gave 1·432 for $\lambda = \infty$; and U. Behn and F. Kiebitz gave 1·47–1·50 for $\lambda = 75$. A. Russell expressed the dielectric properties of air as 38–39 kilovolts per cm.; J. J. Thomson, 30; M. O'Gorman, 27; and C. P. Steinmetz, 38·2. W. Kliefoth observed the **electrostriction**, or contraction in vol., which occurs on applying a powerful electrical field, showing that the attraction between the molecules of air has an electrical origin. Values for the **magnetic susceptibility** of air ranging from $+0{\cdot}024 \times 10^{-6}$ to $+0{\cdot}03085 \times 10^{-6}$ have been reported by G. Quincke,[26] H. du Bois, J. A. Fleming and J. Dewar, P. Curie, R. Hennig, T. Soné, and

W. P. Roop—for air at atm. press. and 16° to 22°; for air at 40 atm. press., G. Quincke gave $1{\cdot}3\times10^{-6}$ mass units; V. I. Vaidyanathan gave $0{\cdot}029\times10^{-9}$ vol. units at ordinary temp. and at a low press.; and for air at 182°, J. A. Fleming and J. Dewar gave $0{\cdot}28\times10^{-6}$ mass units; E. Lehrer, $24{\cdot}16\times10^{-6}$ absolute values; and G. W. Hammar made observations on this subject. W. Schütz, and K. S. Krishnan observed no orientation of the atoms in a magnetic field.

N. T. de Saussure[27] said that 100 vols. of water at 15° absorb about 5 vols. of atm. air at 760 mm. press. The **solubility** of air in *water* has been studied by O. F. Tower, W. Dittmar, E. Wiedemann, W. French and F. Ashworth, K. Angström, W. E. Adeney and H. G. Becker, J. H. Coste, R. Bunsen, H. E. Roscoe and J. Lunt, H. E. Hamberg, H. Tornöe, B. Schulz, and O. Petterson and K. Sondén. J. Metschl discussed supersaturated soln. of air in water. According to L. W. Winkler, 1000 c.c. of water dissolve the proportions of oxygen and nitrogen indicated in Table IX; the air was freed from carbon dioxide and ammonia. The barometer was normal. Nitrogen includes argon and other inert gases. The results of A. Mallet were discussed in **1.** 10, 5. J. Porter measured the solubility of air at normal press. in purified and in alkaline water at various temp. He found that more air remains in the water than corresponds with its solubility, and this air is evolved only when the temp. is raised above 80°. It is suggested that this air is not in an unstable supersaturated condition, but it forms a layer firmly bound to the surface of the vessel so that it has no appreciable vol. This air can be liberated provided the temp. be kept at 60° for 2 or 3 hrs. J. Porter also measured the rate at which air is absorbed from the atm. by de-aerated water. W. Dittmar, H. Tornöe, and H. E. Hamberg examined the solubility of air in sea-water; O. F. Tower, in dil. and conc. *sulphuric acid.*

TABLE IX.—THE SOLUBILITY OF AIR IN WATER.

Temp.	O_2 c.c.	N_2 c.c.	Total c.c.	Per cent. O_2 in dissolved air.	Temp.	O_2 c.c.	N_2 c.c.	Total c.c.	Per cent. O_2 in dissolved air.
0°	10·19	18·99	29·18	34·91	16°	6·99	13·35	20·14	34·31
2°	9·64	18·05	27·69	34·82	18°	6·61	12·77	19·38	34·12
4°	9·14	17·18	26·32	34·74	20°	6·36	12·32	18·63	34·03
6°	8·68	16·38	25·06	34·65	22°	6·11	11·90	18·01	33·95
8°	8·26	15·64	23·90	34·56	24°	5·89	11·49	17·38	33·86
10°	7·87	14·97	22·84	34·47	26°	5·67	11·12	16·79	33·77
12°	7·52	14·35	21·87	34·38	28°	5·46	10·75	16·21	33·68
14°	7·19	13·78	20·97	34·30	30°	5·26	10·38	15·64	33·60

Conc. of H_2SO_4	98	90	80	70	60	50
Solubility	0·0173	0·0069	0·0069	0·0055	0·0059	0·0076

A. von Antropoff found air to be soluble in *aniline* and in *acetic acid;* F. Dolezalek, in *benzene;* and A. Christoff, in *ethyl ether*—such that one vol. of ether absorbs 0·290 vol. of air at 0° and 760 mm.; 0·287 vol. at 10°; and 0·286 vol. at 15°. According to S. Robinet, 100 vols. of 95 per cent. *alcohol* dissolve 14·1 vols. of air; *petroleum,* 6·8 vols.; *benzene,* 14·0 vols.; *oil of lavender,* 6·9 vols.; *oil of turpentine,* 24·2 vols. The **adsorption** of air by *charcoal* has been studied by K. Siebel.[28] F. Bergter, E. Berl and K. Andress, J. Chappius, A. B. Lamb and co-workers, V. Lefebure, S. McLean, H. B. Lemon and K. Blodgett, and A. Piutti; *indiarubber,* by H. A. Daynes, T. Graham, C. G. Hüfner, and V. Lefebure; J. D. Edwards and S. F. Pickering found that if the permeability of rubber for hydrogen is unity, the value for air is 0·22. The adsorption of air by *zeolites* was studied by C. Friedel; *chabasite,* by R. Nacken and L. Wolff, and R. Seeliger; *soils,* by E. Reichardt, and H. E. Patten and F. E. Gallagher; *salts,* by P. A. Guye and N. Zachariades; *silver bromate,* by J. H. Reedy; *silver halides, silver phosphate* and *iodine pentoxide,* by T. W. Richards and G. P. Baxter; *benzoic acid,* and *potassium chloride*, by A. Scott; *copper oxide*, by P. A. Guye and N. Zachariades; and *celluloid, viscose*, or *artificial silk*, and *gelatin*, by V. Lefebure.

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§ 3. The Discovery of Nitrogen

> Le mérite de la découverte d'une vérité appartient tout entier à celui qui la démontre. —P. S. de Laplace.

It is difficult to state precisely who first isolated nitrogen and clearly recognized it as a definite substance. In his experiments on combustion or burning (**1**. 1, 13–16), John Mayow, during his investigation on nitre, got very near, if he did not get actually there. Several others also were not far away from the discovery. As G. F. Rodwell[1] pointed out, the man who deduces on good mental evidence, or even proves by actual experiment, the existence of something not known before is not always recognized as the discoverer ; but rather is hailed discoverer he who proves by a conclusive series of experiments that the substance in question has properties, *sui generis*, distinct from all other substances. *He alone discovers who proves.* Otherwise, Boyle or Paracelsus would be called the discoverer of hydrogen ; Lucretius, of carbon dioxide ; J. Kunckel, of ammonia ; Eck de Sultzbach, of oxygen ; Hooke or Cassini, of the law of gravitation ; etc. D. Rutherford is generally credited with the discovery of nitrogen. It appears that Joseph Black, having noticed that a residue was left after the combustion of carbonaceous bodies in air, and the absorption of fixed air produced by the combustion, suggested to one of his pupils, Daniell Rutherford, the desirability of an investigation on this subject. In 1772, D. Rutherford published a thesis entitled: *Dissertatio inaugauralis de aere fixo dicto aut mephitico* (Edinburgh, 1772), in which he said :

> By the respiration of animals, healthy air is not merely rendered mephitic but it also suffers another change, for after the mephitic portion is absorbed by solution of caustic alkali, the remaining portion is rendered salubrious ; and although it occasions no precipitate in lime water, it nevertheless extinguishes flames, and destroys life.

D. Rutherford thus removed oxygen from the air by such combustibles as phosphorus, charcoal, etc., and washed out the products of combustion by alkali-lye or lime-water. The residue was called by him *phlogisticated air ;* hydrogen was also called phlogisticated air. D. Rutherford believed that nitrogen was produced when the burning body gave up some of its phlogiston to the air ; while hydrogen was produced by the union of phlogiston with atm. air.

In the manuscript papers of H. Cavendish, there is one which he marked " communicated to Dr. Priestley," and which is acknowledged by J. Priestley in his paper on *Airs*. Here, H. Cavendish clearly distinguished nitrogen from other kinds of unrespirable and incombustible gases, and proved by experiment that atm. air consists of two parts, one of which in the combustion of charcoal is converted into fixed air, and the other is a mephitic air *sui generis*. He said :

> The natural meaning of *mephitic air* is any which suffocates animals . . . but in all probability there are many kinds of air which possess this property. . . . I transferred some common air out of one receiver through burning charcoal into a second receiver . . .

the air in the second receiver was passed back again through fresh burning charcoal into another receiver . . . the fixed air formed in each case was absorbed by sope leys. The 180 oz. measures of air in the first receiver was reduced to 162 oz. measures of this mephitic air. The sp. gr. of this air was found to differ very little from that of common air ; of the two it seemed rather lighter. It extinguished flame, and rendered common air unfit for making bodies burn, in the same manner as fixed air, but in a less degree, as a candle which burnt about 80 sec. in pure common air, and which went out immediately in common air mixed with $\frac{6}{55}$th of fixed air, burnt about 26 sec. in common air mixed with the same portion of this burnt air.

H. Cavendish called this residual air *mephitic air*, and added :

In all probability there are many kinds of mephitic air. I am sure there are two—namely fixed air, and common air in which candles have burned, or which has passed through the fire. Air which has passed through a charcoal fire contains a great deal of fixed air which is generated from the charcoal, but it consists principally of common air which has suffered in its nature from the fire.

It is estimated that the nitrogen thus prepared by H. Cavendish contained about one-tenth of carbon monoxide. The portion of the air—oxygen—which has disappeared in this experiment was supposed to have been absorbed by the fumes of the burning charcoal. The recognition of the inert gases in atm. air was discussed in the chapter on the inert gases.

A. L. Lavoisier first called the residual gas *la moufette atmosphérique*, and afterwards *azote;* C. W. Scheele, *verdorbene Luft ;* and J. A. C. Chaptal de Chanteloup suggested the name *nitrogène*—from *νίτρον*, saltpetre ; and *γεννάω*, I produce—because the gas is a constituent of nitre. The Germans call it *Stickstoff*. The term *azote* may be derived from the alchemical term *azoth*—possibly made up from the initial letter *a* of the Latin, Grecian, and Hebraic alphabets, and the last letters of these alphabets—referring to a hypothetical *mercury of wisdom*—whatever that may mean. A. Libavius said that *azoth* may be derived from an old Spanish-Arabian term *azoque* or *azoc* for mercury ; and that the term may even be an abbreviation of *μυστήριον ἄζωτον*, the revealed secret.

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§ 4. The Occurrence of Nitrogen

Nitrogen is the dominant element in air. The gas being a little soluble in water, it is also found dissolved in sea-waters, rivers, and rain-water. Nitrogen also occurs in mineral waters, and in the gases derived from these springs. Thus, R. Bunsen[1] reported 99·5 per cent. nitrogen in the gases from the geysers in North Iceland ; J. L. Smith, 97 per cent. in the gas from the Yalova springs, Asia Minor ; M. Bamberger and A. Landsiedl, 94·83 per cent. in the gases from the Vöslau springs near Vienna ; E. Ludwig, 84·83 per cent. in the gas from Olovo ; P. Bourcet, 61·16 per cent. in the gas from Joule, Jura ; E. Ludwig, 5·44 per cent. in the gas from the springs in the vicinity of Banjaluka ; and F. Ragsby, 0·45 per cent. in the gas from the springs at Mont Dore. Other observations have been made by C. Moureu, A. Purgotti and G. Anelli, C. Bouchard and A. Desgrez, R. Nasini and F. Anderlini, H. Siegmund and P. Juhasz, G. Carrara, E. Ludwig and R. von Zeynek, H. Wurtz, M van Breukcleven, F. Parmentier and A. Hurion.

Variable quantities of nitrogen have been reported in the gases of volcanic origin by T. Schlösing.[2] H. Davy reported nitrogen in the gas from inclusions in rocks. W. F. Hillebrand found the gas occluded in uranite, etc.—*vide* helium. W. N. Hartley, W. A. Tilden, and G. Tschernik found the gas in a number of rocks and minerals—*e.g.* sapphire, topaz, coal, lignite, etc.; A. Gautier, in granite, porphyry, etc.; and C. Erkin, in sandstone, oolites, marls, fuller's earth, etc. A. Delesse reported 0·008 per cent. in green fluorspar; 0·002, in smoky quartz; 0·03, in opal; 0·012, in Iceland opal; 0·007, in chalcedony; 0·004, in emerald; 0·022, in topaz; 0·01, in barytes; 0·026, in gypsum; 0·015, in Iceland spar, and in stalactites; 0·019, in iron spar; and 0·017, in smithsonite. The nitrogen was not an accidental infiltration from the surface. Very little was found in pyroxene, garnet, mica, talc, steelite, and zeolites. J. Parry, and A. H. Allen, etc., showed that iron and steel contain some occluded nitrogen. O. Silvestri reported it occurring as iron nitride in some fresh lava from Etna; and J. B. J. D. Boussingault found it to the extent of 0·011 per cent. in the occluded gas of the meteoric iron from Lenarto.

T. W. Richards found that nitrogen occurs in traces in many oxides prepared by the calcination of nitrates. Nitrogen occurs in numerous chemical compounds —*e.g.* nitrates, ammonium salts, alkaloids, etc. A. F. de Fourcroy[3] found nitrogen in the swimming bladder of the carp. Nitrogen occurs combined in ammonia, nitre, and a great many animal and vegetable products—*e.g.* white of egg, proteids, etc. It is a constant and essential constituent of all living organisms; all life seems to depend upon the transformation of proteid compounds. J. Davidson studied the change in the nitrogen content of wheat seedlings during germination and growth; and R. Combes, the accumulation of nitrogen by the foliage, stem, and roots of a two-year-old beech during 16 months' growth.

C. A. Young, H. Draper, C. Fievez, A. Fowler and C. C. L. Gregory, etc., observed that nitrogen lines occur in the spectrum of the sun; but, as shown by M. N. Saha, the evidence is not conclusive, and he added that although no lines of nitrogen occur in the solar spectrum, the presence of nitrogen is revealed by the existence of cyanogen bands. This question was also discussed by F. E. Baxandall, and W. H. Wright.

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§ 5. The Preparation of Nitrogen

Nitrogen is easily obtained from air by removing the admixed carbon dioxide and oxygen. This is conveniently done by burning a piece of phosphorus in a dry crucible floating on the surface of water under a small bell-jar. The phosphorus combines with most of the oxygen, forming phosphorus pentoxide, and this quickly dissolves in water, leaving behind the nitrogen. If the water be alkaline with sodium hydroxide, the carbon dioxide, normally present in air, will also be removed. The nitrogen so prepared is not pure because the phosphorus ceases to burn before all the oxygen has been removed. A soln. of cuprous chloride in hydrochloric acid rapidly absorbs oxygen from air, and leaves behind the nitrogen—*vide supra*, the analysis of atm. air. It is best to remove the carbon dioxide by first passing the air through a soln. of sodium hydroxide; and to absorb the oxygen by means of an element which will form a non-volatile oxide. C. Brunner,[1] and G. Spencer used red-hot reduced iron. Copper is generally considered best for the purpose; the " turnings " offer a large surface of oxidizable metal to the air. This agent was employed by J. B. A. Dumas and J. B. J. D. Boussingault, R. Bunsen, P. von Jolly, A. Leduc, T. Welton, O. Franke and O. Finke, Cyanid-Gesellschaft, L. Carius, and R. Threlfall. M. Berthelot removed the last traces of oxygen by chromous chloride—*vide supra*—and H. Deslandres by molten sodium. The general process is as follows:

Air freed from carbon dioxide in a wash bottle of sodium hydroxide, *A*, Fig. 3, and from moisture by passage through sulphuric acid, *B*, is then passed through a red-hot tube containing copper turnings. The copper removes the oxygen and forms cupric oxide: $2Cu+O_2=2CuO$. The nitrogen passes on to be collected in a gas jar, or gasholder, etc. In the diagram, the air is supposed to be drawn over the copper, the gasholder being filled with nitrogen. If the gasholder were placed at the end A, and air forced along the tubes, the nitrogen gas could be collected in gas jars, Fig. 3. Cold boiled water should be used in the gasholder so as to lessen the risk of contamination owing to the presence of oxygen dissolved in ordinary water.

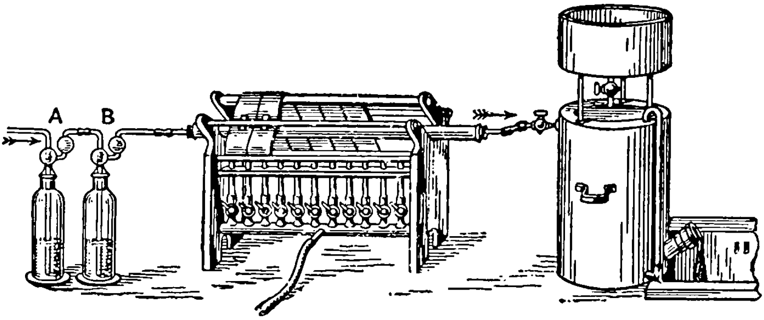

FIG. 3.—Preparation of Nitrogen.

The process of oxidation of course ceases when all the copper is oxidized. If the air, before passing over the red-hot copper, be led through an aq. soln. of ammonia, as recommended by S. Lupton, the ammonia reduces the copper oxide as fast as it is formed: $2Cu+O_2+nN_2=2CuO+nN_2$; and $3CuO+2NH_3=3Cu+3H_2O+N_2$. Any excess of ammonia can be removed by passing the gas from the copper tube through a soln. of sulphuric acid before it is collected in the gasholder. This process was suggested by A. G. V. Harcourt, and used by S. Lupton, H. Biltz, M. Berthelot, R. Threlfall, W. L. Badger, etc. C. van Brunt devised the apparatus illustrated, Fig. 4, for obtaining nitrogen from the air by the copper-ammonia process. A mixture of equal vols. of a sat. soln. of commercial ammonium carbonate and ammonia of sp. gr. 0·93 is introduced into the vessel *A*, and copper turnings in the cylinder *B*. A current of air is directed into the inlet tube, and this ensures the circulation of the liquid in the apparatus *viâ C*, the speed of flow of the liquid being regulated by the clamp *D*. The air discharged in the cylinder *B* is freed from oxygen by the copper and ammonia. The ammonia is removed from the nitrogen by scrubbing the gas from the exit tube with dil. sulphuric acid. W. L. Badger modified the apparatus using also a soln. of ammonia sat. with ammonium chloride.

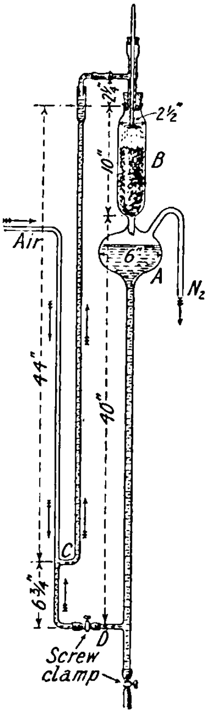

FIG. 4.—Nitrogen by the Ammonia-Copper Process.

G. A. Hulett passed a mixture of hydrogen and air over heated copper; and observed that the hydrogen reduced the copper oxide as fast as it was formed: $2Cu+2H_2+O_2+nN_2=2Cu+2H_2O+nN_2$. A number of processes have been devised—by A. Frank and N. Caro,[2] D. Lance and E. G. Elworthy, J. D. Riedel, H. Braun, J. Harger, the Société l'Oxyhydrique Française, F. A. Rudolf, the Cyanid-Gesellschaft, C. E. Acker, etc.—for removing the carbon dioxide and water from flue gases, etc., so as to leave the nitrogen as a residue. E. Romanelli burnt hydrogen in air to remove the oxygen; the Elektrizitätswerk Lonza used ammonium hydrosulphite as absorbent, followed by combustion with hydrogen. F. J. Metzger obtained nitrogen—free from oxygen—for annealing metals, etc., by adding a combustible gas—*e.g.* hydrogen—and bringing the mixture under high press. in contact with carborundum at about 400° so as to maintain the combustion of the combustible gas with oxygen. The combustion products are then separated by condensation. J. E. Bucher described a process in which coke-oven gas is passed over copper at 450°. The oxygen forms copper oxide which is subsequently reduced by the coke-oven gas. G. Kassner removed the oxygen from air by absorption with calcium plumbite, alkali manganite, etc. H. Kautsky and H. Thiele forced air through a porous membrane in a soln. of sodium hyposulphite when all but 0·0007 per cent. of oxygen was removed from the nitrogen. V. Oehlmann removed the oxygen by passing air over pieces of calcium sulphide moistened with a soln. of an iron salt.

The preparation of nitrogen by the fractional distillation of liquid air was discussed in the first volume (**1**. 13, 25). Several processes for conducting this operation have been patented.[3] G. J. Merturi separated the components of air by diffusion through rubber, etc.—*vide* atmolysis. Nitrogen obtained from the atmosphere is, of course, contaminated with argon and the inert gases. This is not the case with nitrogen from compounds containing the gas in combination with other elements. In 1789, A. F. de Fourcroy [4] noted that when chlorine gas is passed into an excess of aq. ammonia, nitrogen is evolved; if the ammonia be not in excess, the violent explosive nitrogen chloride (*q.v.*) is formed. A. Anderson said that the product is always contaminated with oxygen. If a soln. of aq. ammonia or ammonium salt be treated with a hypochlorite or hypobromite, nitrogen is again produced. A. Fauconnier said that in this reaction a part of the ammonia is converted into nitrous acid. In conducting the process, a soln. of ammonia is treated with bleaching powder in soln. or, as recommended by G. Neumann, compressed into cubes. F. C. Calvert used 200 c.c. of a soln. of bleaching powder containing 5 per cent. of hypochlorite, and mixed with 1·146 grms. of ammonium sulphate. E. Marchand employed ammonium chloride in place of the sulphate. H. P. Waran made nitrogen by dropping bromine into aq. ammonia. Lord Rayleigh found that a trace of nitrous oxide is always formed when nitrogen is prepared by the action of hypobromites or hypochlorites on urea, or other acid amides. F. C. Calvert noted the formation of nitrogen when organic substances, like gelatine, albumin, glue, soap, etc., are treated with hypochlorites. G. J. Fowler observed that nitrogen is formed when iron nitride is treated with chlorine. D. Chattaway and K. J. P. Orton found that a soln. of nitrogen iodide in an organic solvent decomposes with the evolution of nitrogen; and that the nitrogen hydroiodides furnish the same gas when exposed to light, or treated with water or alkali-lye.

B. Corenwinder[5] showed that when an aq. soln. of ammonium nitrite is heated, nitrogen gas is evolved: $NH_4NO_2=2H_2O+N_2$; better results are obtained with a mixture of ammonium chloride and a conc. soln. of alkali nitrite. The product always contains a trace of nitric oxide, and O. W. Gibbs stated that this contamination can be avoided by washing the gas with an excess of a conc. soln. of potassium dichromate and acetic acid which converts the impurity into nitric acid. J. P. Emmet added a piece of zinc to molten ammonium nitrate and obtained a brisk evolution of nitrogen. C. Winkler found that when a mixture of ammonium nitrate and phosphorus is heated, nitrogen is evolved: $2P+5NH_4NO_3=2H_3PO_4+5N_2+7H_2O$. E. J. Maumené warmed a mixture of ammonium nitrate and chloride and washed out the chlorine from the mixture of gases which was evolved; E. Soubeiran employed a mixture of potassium nitrate and ammonium chloride. J. W. Gatehouse heated a mixture of ammonium nitrate and manganese dioxide to 180° and obtained nitrogen gas; if the temp. rises over 215°, the manganese nitrate which is formed decomposes, giving off oxygen, nitrogen, and nitrogen peroxide. A. Levy made nitrogen by heating ammonium dichromate: $(NH_4)_2Cr_2O_7=Cr_2O_3+4H_2O+N_2$; and R. de Luna recommended a mixture of potassium dichromate and ammonium chloride, and washing the gas with a soln. of ferrous sulphate. R. Böttger, and C. L. Jackson and J. H. Derby heated a mixture of potassium dichromate, sodium nitrite, ammonium nitrate, and water, and V. Meyer recommended removing oxygen from the product by passing the gas over heated copper; G. von Knorre used an analogous mode of preparation and found that the use of an acidified soln. of a ferrous salt to remove the nitrogen oxides is objectionable because the absorbed nitric oxide is given off again as the nitrogen passes through the soln., and an acidified soln. of potassium permanganate converts the nitric oxide into nitric acid which reacts with the permanganate, giving off oxygen. C. R. C. Tichborne made nitrogen by heating a mixture of ammonium sulphate, sodium nitrite, and an aq. soln. of glycerol; and J. Mai heated a mixture of glycerol, dil. sulphuric acid, and ammonium nitrate to 165°. The reaction is said to commence at 190°, but once started the reaction proceeds at 150°. A few drops of sulphuric acid cause the reaction to proceed more regularly at a lower temp. The gas is said to be evolved regularly, and to be contaminated with oxygen, carbon dioxide, and pyridine bases. S. M. Delépine found that when spongy platinum is boiled with ammonium sulphate and sulphuric acid, nitrogen and sulphur dioxide are formed: $4H_2SO_4+Pt=Pt(SO_4)_2+2SO_2+4H_2O$; and $3Pt(SO_4)_2+2(NH_4)_2SO_4=2N_2+3Pt+8H_2SO_4$. C. W. Geuns observed some nitrogen is formed when a mixture of potassium cyanide and potassium nitrite is detonated by heat. J. Pelouze obtained nitrogen by adding ammonium sulphate to a sat. soln. of nitric oxide in sulphuric acid, and heating the mixture to 160°. According to G. P. Baxter and C. H. Hickey, pure nitrogen can be readily obtained in large quantities by the interaction of nitric or nitrous oxide and ammonia at a high temp. In the case of nitric oxide, the following method is employed. The gas, generated by the action of nitric acid of sp. gr. 1·2 on copper turnings, is led through a wash-bottle containing strong ammonia soln., and afterwards over hot copper gauze or thoroughly platinized asbestos. The nitrogen thus obtained is passed through dil. sulphuric acid, and afterwards over fused potassium hydroxide, through a tower containing glass beads moistened with strong sulphuric acid, and finally through a small tube containing a roll of red-hot copper gauze. The sp. gr. of ammonia soln. for this purpose must not be higher than 0·92. In the case of nitrous oxide, the gas obtained by heating ammonium nitrate is passed over red-hot platinized asbestos, then into a wash-bottle containing strong ammonia soln., and again over heated platinized asbestos. G. von Knorre and K. Arndt obtained nitrogen by oxidizing hydroxylamine with an acid soln. of an alkali nitrate in the presence of cupric sulphate, mercuric chloride, ammonium persulphate, hydrogen dioxide, or vanadium pentoxide; with the last-named catalyst, some nitrous oxide is also produced. E. C. Szarvasy obtained nitrogen in the electrolysis of hydrazine and of its salts; and E. Tiede obtained nitrogen of a high degree of purity by the slow decomposition of azides in vacuo.

Nitrogen is formed in a number of reactions with organic compounds. F. Hoppe-Seyler,[6] L. Liebermann, M. Grüber, M. Pettenkofer and C. Voit, T. Schlösing and A. Müntz, A. Morgen, G. van der Velde, H. B. Gibson, and J. Seegen and J. Nowak, noticed that when fibrin, and some proteids are decomposed, hydrogen sulphide, carbon dioxide, and nitrogen may be formed. The reduction of organic substances in soils to nitrogen gas was indicated by H. Davy in 1813. Confirmatory observations were made by G. J. Mulder, B. E. Dietzell, O. Kellner and T. Yoshii, B. Tacke, and C. Oppenheimer. The reduction of nitrates to nitrogen by bacteria was first reported by U. Gayon and G. Dupetit in 1886, and since that time numerous observations have been made. A. Ambroz, G. Ampola and E. Garino, E. Baur, A. Boutron, K. Brandt, E. Bréal, R. Burri and A. Stutzer, H. R. Christensen, A. Ehrenberg, P. F. Frankland, E. B. Fred, E. Giltay and G. Aberson, A. Gehring, L. Grimbert, and M. Bagros, W. Henneberg, H. Immendorff, H. Jensen, H. Kühl, O. Künnemann, O. Lemmermann, M. Lemoigne, J. Leone, R. Lieske, W. C. C. Pakes and W. H. Jollyman, D. Parlandt, J. Schirokikh, T. Schlösing, S. A. Sewerin, J. Stoklasa, J. Vogel, P. Wagner, R. Warington, O. Wegner, H. Weisenberg, and P. P. Déhérain and L. Maquenne, noted the formation of nitrogen during the reduction of nitrates by bacteria; and E. Buchner and R. Rapp, and B. E. Dietzell, in the reduction of nitrites by yeast. H. Leo found that only a very small liberation of nitrogen occurs during the assimilation of food by flesh-eating organisms. G. Ampola and C. Ulpiani[7] showed that the denitrifying bacteria—*bacterium denitrificans,* etc.—does not attack asparagine, or nitromethane; and with ethyl nitrate the action is slow. The nitrates of lithium, ammonium, sodium, potassium, rubidium, cæsium, beryllium, silver, thorium, yttrium, iron, manganese, and aluminium are not attacked· The more electropositive the metal and the lower its at. wt., the more rapidly does denitrification take place. Carbamide nitrate, which is only slightly dissociated in soln., is slowly attacked, whilst with the nitrates of strychnine, brucine, cocaine, and pilocarpine, which are entirely ionized in soln., denitrification is soon complete. The bacteria do not develop in soln. of metallic chromates, and only to a small extent in soln. of bromates or iodates; chlorates, arsenates, and ferricyanides suffer reduction, but sulphates, phosphates, and molybdates remain unchanged. Calcium nitrate is much less readily attacked than sodium nitrate. M. E. Wollny, and B. Tacke found that in some cases nitrous oxide is formed as well as nitrogen. This was confirmed by M. W. Beyerinck and D. C. J. Minkman, and S. Suzuki. Again, B. Tacke, and A. J. Lebedeff found that nitric oxide is formed by the action of *bacterium hartlebii* on nitrate soln.

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§ 6. The Physical Properties of Nitrogen

At ordinary temp., nitrogen is a colourless, odourless, tasteless gas which has no action on vegetable colouring matters. H. Erdmann[1] described liquid nitrogen as a clear, colourless, mobile liquid. J. de Smedt and W. H. Keesom found that the **X-radiograms** of solid nitrogen show that the symmetry of the crystals is less than that of the cubic system. D. Vörlander and W. H. Keesom found that the crystals which form when nitrogen is cooled to —210° are doubly refracting. Contrary to W. Wahl, no isotropic solid state was observed when the solid is cooled down to —253°. The gas is not quite so heavy as air. According to H. V. Regnault, **the weight of a litre** of nitrogen is 1·256167 grms. at 0° and 760 mm.; J. M. Crafts, 1·25647 grms.; P. von Jolly, 1·2574614 grms. at 0°, 760 mm., latitude 45°, and sea-level; Lord Rayleigh, 1·2578731 grms.; and A. Jaquerod and F. L. Perrot, 1·25045 grms. at 0°, and 0·25451 grm. at 1067·4°. M. Paya and E. Moles found 1·25681 grms. for the nitrogen of the air of Madrid—*vide supra*, atmospheric air. Lord Rayleigh obtained a greater value for nitrogen separated from atm. air than from nitrogen prepared from chemical compounds; and Lord Rayleigh and W. Ramsay demonstrated that the result was due to the presence of a heavier gas in atm. nitrogen—*vide* argon. A litre of purified nitrogen was found, by Lord Rayleigh and W. Ramsay, to weigh 1·2505 grms. under standard conditions; and by A. Leduc, 1·2507 grms. E. Moles and J. M. Clavera gave 1·2505 grms. for the nitrogen of air at 0°, 760 mm., and latitude 45°. C. J. T. Hanssen, and J. K. H. Inglis and J. E. Coates made observations on this subject. G. P. Baxter and H. W. Starkweather gave 0·41667, 0·83348, and 1·25036 at 0° and the respective press. 253·33, 506·67, and 760 mm., at sea-level, and latitude 450'. For the **relative density** of atm. nitrogen (air unity), P. L. Dulong and J. J. Berzelius gave 0·968; J. B. A. Dumas and J. B. J. D. Boussingault, 0·972; T. Thomson, 0·9729; H. V. Regnault, 0·97137; J. M. Crafts, 0·97138; A. Leduc, 0·972; and Lord Rayleigh, 0·97209. For purified nitrogen, Lord Rayleigh gave 0·96727; A. Leduc, 0·9671; T. Schlösing, 0·9671; and P. A. Guye, 14·007(H=1·0077). J. K. H. Inglis and J. E. Coates gave 0·8084 at —193·93° and 0·8297 at —195·5°; while E. C. C. Baly and F. G. Donnan gave 0·8010 at —193° and 0·8218 at —198°. The literature was reviewed by M. S. Blanchard and S. F. Pickering. The molecule of nitrogen is diatomic, N_2, and, according to V. Meyer and co-workers, no perceptible dissociation occurs at 1690°.

E. Gerold gave for the **specific gravity,** D, of gaseous nitrogen D=0·0044973 at —195·5° and 741·10 mm. The sp. gr. of liquid nitrogen was found by S. von Wroblewsky to be 0·4552 at —146·6°/4°; 0·5842 at —153·7°/4°; 0·8300 at —193·0°/4°; and 0·8660 at —202·0°/4°. J. Dewar gave 0·8042 at —195·5°, and 0·8792 at —252·5°; J. Drugman and W. Ramsay, 0·7914 at —195·5°; and L. Grunmach, 0·791 at —195·9°. E. C. C. Baly and F. G. Donnan represented the sp. gr., D, of liquid nitrogen, between —184° and —205°, by $D=0·853736-0·00476(T-68)$. They found:

	—205°	—200°	—195°	—190°	—185°
D	0·8537	0·8309	0·8080	0·7851	0·7622

E. Mathias and co-workers have determined the density of liquid nitrogen and of the sat. vap. over the range of temp. between the solidification point and the critical point, and have compared the values with the results already obtained for argon and oxygen. Leaving out the values for the three degrees below the critical temp., the values for the density of nitrogen deviate but very slightly from a straight line, which, however, shows a convex curvature towards the temp. axis at the low temp. Solid nitrogen was found by J. Dewar to have a sp. gr. of 0·8792 at —210·5°, and 1·0265 at —252·5°. E. Rabinowitsch gave 35·4 for the mol. vol.; and the subject was studied by P. N. Pavloff, C. del Fresno, S. Sugden, W. Herz, S. Mokruschin, and C. E. Guye and R. Rudy. I. I. Saslawsky gave 1·12 for the sp. gr., and 10·3 for the at. vol. at absolute zero; and F. Schuster, 10·63 at the b.p. as the constant for calculating the mol. vol. of compounds.

L. Cailletet[2] measured the **compressibility** of nitrogen at 15°, and found the product *pv*, to be:

p .	39·359	49·271	59·462	74·330	114·119	181·985 m.
v .	207·93	162·82	132·86	108·86	76·69	51·27
pv .	8184	8022	7900	8091	8751	9330

E. H. Amagat's results are given in Table X. There is a minimum value for the product *pv* with a press. of 5 m. of mercury. M. W. Travers gave:

p . .	0·76	10	25	35	45	55	65 m.
pv . .	1·0000	0·9963	0·9910	0·9899	0·9895	0·9902	0·9913

The coeff. of compressibility was found by E. H. Amagat to decrease with increasing press.:

Limits of press. .	750–1000	1000–1500	1500–2000	2000–2500	2500–3000 m.
Coefficient . .	0·000407	0·000265	0·000170	0·000122	0·000091

Lord Rayleigh's value for the ratio of *pv* at one atm. press. to its value at half an atm. press. is 1·000015. L. Holborn and J. Otto measured the low temp. isotherms, and found $pv=2{\cdot}46558+1{\cdot}38086p+0{\cdot}8082p^2$ at 400°; $pv=1{\cdot}36682+0{\cdot}36057p+3{\cdot}1510p^2$ at 100°; $pv=1{\cdot}00060-0{\cdot}60716p+3{\cdot}7959p^2$ at 0°; and $pv=0{\cdot}52446-4{\cdot}68594p-24{\cdot}4699p^2$ at —130°. E. H. Amagat showed that the ratio p_0v_0/p_1v_1 is 0·909 between 60 m. and 180 m. press., and Boyle's law is applicable up to 300 m. press. J. A. Liljeström found that for press. below atm. deviations occur. G. P. Baxter and H. W. Starkweather obtained $pv=1{\cdot}00011$ and 1·00028 respectively for press. $\frac{2}{3}$ and $\frac{1}{3}$ atm. when the value for 1 atm. press. is unity. P. de Heen said that if allowance be made for the vol. of the mols., Boyle's law is closely followed by nitrogen. L. B. Smith and R. S. Taylor calculated the compressibility to be 0·000608 at 0°, 0·000216 at 50°, and —0·000071 at 100°; P. Chappius, 0·00043; G. M. Maverick, 0·00044; A. Leduc and P. Sacerdote, 0·00038; Lord Rayleigh, 0·00056; and J. Holborn and J. Otto, 0·000561 at 0°, 0·00023 at 50°, and —0·000360 at 100°. E. Cardoso and T. Levi found for nitrogen at 16° the following values of *K* in the expression $p=Kp_0v_0T/vT_0$:

$p_{atm.}$ . .	1	10	20	40	60	80	95
K . . .	1·0000	0·9971	0·9939	0·9898	0·9887	0·9902	0·9929
K (Amagat) .	1·0000	0·9971	0·9945	0·9907	0·9896	0·9908	0·9930

Observations are also made by H. K. Onnes, T. T. H. Verschoyle, and A. W. Witkowsky. E. P. Bartlett gave for $p_0v_0=1$ at 0° and 1 atm. press., and

p . .	50	100	200	400	600	800	1000
pv/p_0v_0 .	0·9839	0·9840	1·0330	1·1250	1·5211	1·7985	2·0659

E. P. Bartlett concluded that the compressibility of mixtures of hydrogen and nitrogen is not a linear function of its composition. A maximum positive deviation of 1·9 per cent. was observed in a mixture containing 60 per cent. of hydrogen at 200 atm. press. A maximum negative deviation of 0·55 per cent. appears in a mixture containing 25 per cent. of hydrogen at 1000 atm. press.

H. K. Onnes and A. T. van Urk measured the isothermal values of *pv* at 20°, 0°, —23·62°, and intermediate temp. down to —146·32°. P. W. Bridgman found for the press., *p* in kgrms. per sq. cm.; the vol., *v* c.c. per gram of nitrogen, at 68°;

the product pv, where v represents the vol. of nitrogen which under 1 kgrm. press. per c.c. at 0° occupies 1 c.c.; and δv the change in vol. per gram:

p	2500	3000	5000	7000	9000	11,000	13,000	15,000
v	1·356	1·290	1·138	1·056	1·003	0·964	0·933	0·908
pv	4·11	4·68	6·89	8·95	10·94	12·84	14·70	16·50
δv	—0·066	0	0·152	0·234	0·287	0·326	0·357	0·382

TABLE X.—E. H. AMAGAT'S VALUES OF pv FOR NITROGEN.

p Atm.	0°		16·03°		95·45°		109·50°	
	pv	v	pv	v	pv	v	pv	v
1	1·0000	1·000000	—	—	—	—	—	—
100	0·9910	0·009910	1·0620	0·010620	—	—	—	—
150	1·0085	0·006723	1·0815	0·007210	1·4500	0·009666	1·8620	0·001241
200	1·0390	0·005195	1·1145	0·001572	1·4890	0·007445	1·9065	0·009532
250	1·0125	0·004330	1·1575	0·004630	1·5376	0·006150	1·0585	0·007834
300	1·1360	0·003786	1·2105	0·004035	1·5905	0·005301	2·0145	0·006715
350	1·1950	0·003414	1·2675	0·003621	1·6465	0·004703	2·0703	0·005923
400	1·2570	0·003142	1·3290	0·003322	1·7060	0·004265	2·1325	0·005330
450	1·3230	0·002940	1·3946	0·003098	1·7665	0·003924	2·1940	0·004875
500	1·3900	0·002780	1·4590	0·002918	1·9275	0·003655	2·2570	0·004514
550	1·4585	0·002652	1·5265	0·002775	1·8960	0·003436	2·3200	0·004218
600	1·5260	0·002543	1·5945	0·002657	1·9545	0·003258	2·3840	0·003973
650	1·5935	0·002452	1·6615	0·002556	2·0200	0·003108	2·4485	0·003613
700	1·6615	0·002374	1·7290	0·002470	2·0865	0·002980	2·5125	0·003589
750	1·7300	0·002307	1·7975	0·002397	2·1535	0·002871	2·5765	0·003435
800	1·7980	0·002247	1·8655	0·002332	2·2200	0·002775	2·6400	0·003300
850	1·8660	0·002195	1·9330	0·002274	2·2865	0·002690	2·7060	0·003184
900	1·9340	0·002149	2·0015	0·002224	2·3540	0·002616	2·7715	0·003079
950	2·0015	0·002107	2·0690	0·002178	2·4230	0·002550	2·8380	0·002987
1000	2·0685	0·002068	2·1360	0·002136	—	—	—	—

O. E. Meyer[3] calculated for the **viscosity** of the gas at 10°–20°, $\eta=0{\cdot}000184$; and O. E. Meyer and F. Springmühl, $\eta=0{\cdot}000194$. T. Graham gave $0{\cdot}0_31635$ at 0°; and $0{\cdot}0_31840$ at 20°; and A. von Obermayer gave $0{\cdot}0_31563$ at —21·5°, and $0{\cdot}0_31894$ at 53·5°. For chemical nitrogen, H. Markowsky gave $0{\cdot}0_31674$ at 0°; $0{\cdot}0_31747$ at 15·4°; and $0{\cdot}0_32123$ at 100·08°; and F. Kleint, $0{\cdot}0_31737$ at 13·9°; $0{\cdot}0_32125$ at 99·5°; and $0{\cdot}0_32460$ at 182·7°. For atm. nitrogen, H. Markowsky gave $0{\cdot}0_31695$ at 0°; $0{\cdot}0_31738$ at 14°; and $0{\cdot}0_32464$ at 183·0°. R. S. Edwards and B. Worswick gave $\eta=0{\cdot}0_4944$ at 10° and $0{\cdot}0_31295$ at 100°, and they found 377 for the value of Sutherland's constant; and K. L. Yen, 0·000176480 at 23° and 760 mm. J. H. Jeans gave $\eta=\eta_0(T/273)^{0{\cdot}74}$. A. Bestelmeyer, and C. J. Smith also made observations on this subject. H. Vogel, S. Chapman and W. Hainsworth, M. Hofsäss, and F. Kleint measured the viscosity of mixtures of hydrogen and nitrogen and of oxygen and nitrogen. F. Schuster calculated 846 atm. for the **internal pressure.** L. Grunmach gave $\sigma=8{\cdot}51$ dynes per cm. for the **surface tension** of liquid nitrogen at —195·9°; and for the **specific cohesion,** $a^2=21{\cdot}527$ sq. mm. E. C. C. Baly and F. G. Donnan gave $\sigma=10{\cdot}53$ at —203°, 8·27 at —193°, and 6·16 at —183°; and $a^2=2{\cdot}541$ at —203°, 2·110 at —193°, and 1·663 at —183°. They added that the association factor of the liquid corresponds with a mol. wt. of 37·30; the theoretical value for N_2 being 28. A. T. van Urk studied this subject. W. D. Harkins and L. E. Roberts estimated that the free **surface energies** at —200°, —190°, and —182° are respectively 10·53, 8·27, and 6·57 ergs per sq. cm., or 26·63, 25·87, and 24·61 ergs per area of surface occupied by one mol.; the energy, $3{\cdot}23\times10^{-16}$, $3{\cdot}24\times10^{-16}$, and $3{\cdot}18\times10^{-16}$ ergs per degree per area occupied by one mol.; and each c.c. of liquid holds $18{\cdot}27\times10^{21}$, $17{\cdot}28\times10^{21}$, and and $16{\cdot}49\times10^{21}$ mols. F. de Block represented the surface tension at θ° by the general formula of A. Ferguson, and J. D. van der Waals, namely, $\sigma=\sigma_0(\theta_c-\theta)^{1{\cdot}282}$, where θ_c represents the critical temp., and σ_0 the surface tension at 0°. T. Alty studied the phenomena at the surface of bubbles of nitrogen in water. The coeff. of **diffusion** of nitrogen into oxygen was found by A. von Obermayer to be 0·171 sq. cm. per sec. at 0°, and O. Jackmann,[4] 0·203 sq. cm. per sec. at 12·5° and 755·6 mm. The latter gave for hydrogen into nitrogen, 0·739 sq. cm. per sec. at 12·5° and 755·4 mm. The diffusion of mercury and iodine vapours in nitrogen have been studied by J. M. Mullaly and H. Jacques. J. Stefan found that nitrogen diffuses in water and in alcohol more quickly than carbon dioxide and more slowly than hydrogen. G. Hüfner gave 1·73 sq. cms. per day for the speed of diffusion of nitrogen towards oxygen in aq. soln. at 21·7°. According to M. Berthelot, nitrogen diffuses through quartz glass at 1300°. T. L. Ibbs studied the separation of nitrogen from hydrogen and from carbon dioxide by thermal diffusion. J. Dewar found that nitrogen, at atm. press. and 15°, diffused through rubber 0·01 mm. thick at the rate of 1·38 c.c. per sq. cm. per day. H. A. Daynes also measured the diffusion of nitrogen in rubber. J. Sameshima and K. Fukaya studied the atmolysis of nitrogen; and T. L. Ibbs and L. Underwood, the thermal diffusion of nitrogen and carbon monoxide.

O. Buckendahl[5] found the **velocity of sound** in nitrogen to be 337·30 metres per sec. at 0°; 544·98, at 500°; and 714·83, at 960°. H. B. Dixon and co-workers made analogous observations between 0° and 100°. The observed values at 0° range from 337·3 to 338·7 metres per sec. They gave for the dry gas:

	20°	42°	62°	77°	80°	86°	90°
Metres per sec. .	339·5	352·9	364·1	372·3	373·9	376·9	378·9

They also measured the velocity of sound in mixtures of nitrogen with carbon dioxide, etc.

The **molecular velocity** of nitrogen at 0° was calculated by F. Kleint[6] to be 45,430 cms. per sec.; the mean **free path**, $0{\cdot}0_5949$ cm. at 0° and 760 mm.; the total sectional area of all the mols. in 1 c.c. of gas at 0° and 760 mm., 24,400 sq. cms., and with W. Sutherland's correction, 17,000 sq. cms.; and the **molecular diameter,** 28×10^{-9} cm. For the mol. diameter, F. Exner gave 17×10^{-9} cm.; S. Mokroushin, $1{\cdot}0\times10^{-8}$ to $6{\cdot}7\times10^{-8}$ cm.; H. Sirk, $3{\cdot}1\times10^{-8}$ to $3{\cdot}9\times10^{-8}$ cm.; W. H. Kecsom, $26{\cdot}5\times10^{-9}$ cm.; J. P. Kuenen, $3{\cdot}1\times10^{-8}$ cm.; and P. Walden, $2{\cdot}9\times10^{-8}$ cm.; W. L. Bragg calculated 1·30 A. for the at. diameter, and A. O. Rankine's estimate agrees with this; W. Sutherland, 30×10^{-9} cm.; P. W. Bridgman, $3{\cdot}56\times10^{-8}$ to $3{\cdot}80\times10^{-8}$ cm.; and R. Rühlmann, $34{\cdot}1\times10^{-9}$ cm. J. H. Jeans, E. Brüche, C. Ramsauer, L. L. Nettleton and W. Schütz made some observations on this subject. H. Schmidt gave 1·035 (oxygen unity). C. J. Smith calculated the mean collision area to be $0{\cdot}767\times10^{-15}$ sq. cm.; and R. S. Edwards and B. Worswick, $0{\cdot}633\times10^{-15}$ sq. cm. A. Naumann calculated the mol. cross-section to be 1·88 with that of hydrogen unity; and the mol. radius, 1·307 (hydrogen unity). W. H. Keesom calculated $4{\cdot}77\times10^{-14}$ ergs for the potential energy of the molecules in contact; and for the quadruple moment $3{\cdot}86\times10^{-26}$ C.G.S. units per sq. cm. R. T. Birge discussed the law of force and size of the diatomic molecules; E. Blankenstein, the coeff. of slip, and transfer of momentum; and A. T. van Urk, the cohesion forces of the liquid. R. Gans discussed the structure of the molecules of the gas. For **J. D. van der Waals' constants,** E. Häntzschel gave $b=0{\cdot}001763$. F. Guye and L. Friedrich gave in gram units $a=1660$ to 1770; and $b=1{\cdot}32$ to 1·51; in mol units, $a=1{\cdot}30\times10^{-6}$ to $1{\cdot}39\times10^{-6}$, and $b=37{\cdot}1$ to 39·5; and in terms of the initial vol., $a=0{\cdot}00276$ to 0·00260, and $b=0{\cdot}00166$ to 0·00176. J. J. van Laar calculated $b=0{\cdot}00085$; $\sqrt{a}=0{\cdot}029$; and the valency attraction A, $\sqrt{A}=32$. M. F. Carroll studied the **equation of state.** F. G. Keyes gave for the equation of state $p=2{\cdot}9138(v-\delta)^{-1}T^{-1}-1587(v-0{\cdot}007)\ ^{2}$, where $\log_{10}\delta=0{\cdot}2200-0{\cdot}284v^{-1}$ for E. H. Amagat's data between 100 and 1000 atm., and $p=2{\cdot}9286(v-\delta)^{-1}T^{-1}-1623{\cdot}6(v+0{\cdot}2954)^{-2}$, where $\log_{10}\delta=0{\cdot}18683\quad 0{\cdot}3113v^{-1}$, for L. B. Smith and R. S. Taylor's data over a smaller range of press.

P. W. Bridgman did not obtain good results for his high press. observations with these formulæ. R. Becker applied to E. H. Amagat's results the equation $p=8{\cdot}31\times10^7T(1+40{\cdot}3v^{-1}e^{40{\cdot}3/v})-1{\cdot}26\times10^{12}v^{-2}+384\times10^{17}v^{-7}$, where p is expressed in dynes per sq. cm. and v in c.c. per mol. P. W. Bridgman obtained better results with this equation than with any other tried when applied to his high press. observations. A. T. van Urk found that the curves show a bend in the neighbourhood of the critical temp. and density. R. Bartels and A. Eucken gave the equation of state $pv=nRT(1-Bp)$, where $B=0{\cdot}0022+19600T^{-2}$ for low temp. and small press.; and T. T. H. Verschoyle, $pv=1{\cdot}00049-0{\cdot}0004961p-0{\cdot}0_5334p^2$ for nitrogen at 0°, and for a 50 per cent. mixture with hydrogen $pv=0{\cdot}99969+0{\cdot}0003067p+0{\cdot}0_51147p^2$. W. J. Walker discussed this subject. R. Becker, and J. E. L. Jones and W. R. Cook studied the *intermolecular attraction —vide infra*, electrostriction—and F. G. Keyes and R. S. Taylor, the effect of *molecular aggregation* on the equation of state. M. Trautz and O. Emert, F. Braun, P. Sacerdote, and A. Leduc investigated the application of the partial press. law to mixtures of nitrogen with hydrogen, oxygen, carbon dioxide, and sulphur dioxide. W. Nernst gave 2·6 for the **chemical constant** of nitrogen; J. R. Partington, 0·904; and F. A. Henglein, and A. Langen, —0·05. W. Herz discussed this subject. A. Eucken and co-workers gave —0·11 for the integration constant of the thermodynamic vap. press. equation. The subject was discussed by R. R. S. Cox.

P. von Jolly [7] found the coeff. of **thermal expansion** of nitrogen to be 0·0036677 at one atm. press. between 22° and 98°. A. Jacquerod and F. L. Perrot gave 0·0036643 from 0° to 1067° when the initial press. was 240 mm. and the vol. was kept constant. P. Chappius found the mean coeff. at constant vol. between —20° and 0° to be 0·000367713 (1002 mm.); between 0° and 20°, 0·000367641 (1002 mm.); between 0° and 40°, 0·000367567 (1002 mm.); and between 0° and 100°, 0·0003677466 (1002 mm.). V. and C. Meyer measured the expansion up to 1567°. E. C. C. Baly and W. Ramsay gave 0·003021 at 0·6 mm. (constant vol.) from 13° to 132°, and 0·003290 at 5·3 mm. and 9° to 133°; H. V. Regnault, 0·0036682 at one atm.; P. Chappius, at 1002 mm. press. (constant), 0·0036770 at 0° to 20°; 0·0036750 at 0° to 40°; 0·0036732 at 0° to 100°; and 0·0036778 at 0° to 100° and a constant press. of 1387 mm. F. Henning and W. Heuse gave for the vol. expansion coeff., $\alpha\times10^7=36604+127p_0$; and for the press. expansion coeff., $\beta\times10^7=36604+134p_0$. According to E. H. Amagat, for a constant press., p, between 0° and 16°, the coeff. of expansion, α, is

p .	100	500	1000	1500	2000	2500	3000 atm.
α .	0·00447	0·00310	0·00198	0·00149	0·00127	0·00111	0·00098

between 0° and 99·4°, and 99·4° and 199·5°:

	0° to 99·4°				99·4° to 199·5°			
p . .	200	500	700	900	200	500	700	900
α . .	0·00433	0·00315	0·00256	0·00218	0·00280	0·00235	0·00204	0·00179

At a constant vol., v, between the indicated temp., he also found:

	0° to 16°			0° to 99·4°			99·4° to 199·6°		
p .	100	1000	2800	100	300	500	100	200	400
β .	0·00437	0·00550	0·00424	0·00462	0·00582	0·00596	0·00315	0·00349	0·00364

R. Plank has collated the available press., temp., and vol. data for nitrogen at a low temp. S. von Wroblewsky gave 0·0311 for the coeff. of expansion of the liquid at —153·7°; 0·007536 at —193·0°; and 0·004619 at —202·0°. E. C. C. Baly and F. G. Donnan gave 0·00558 between —184° and —205°. W. Mewes discussed the deviations from Charles's law; and W. Herz, the relation between the internal press. and the thermal expansion.

A. Winkelmann [8] gave for the **thermal conductivity** of nitrogen gas, 0·0000524 cals. per sq. cm. per cm. per degree at 8° ; P. Günther gave 0·00005694 at 0° ; and S. Weber, 0·00005660 ; E. Schreiner gave for the mol. heat conductivity $2·79\times10^{-6}(273/T)^{\frac{1}{2}}$.

A. Crawford [9] attempted, in 1779, to determine the **specific heat** of nitrogen. This constant was found by F. de la Roche and J. E. Bérard to be $c_p=0·2754$; and by H. V. Regnault to be 0·244 between 0° and 200°. A. K. W. Sauerman gave 1·0005 for the ratio c_p/c_v for air. K. Scheel and W. Heuse gave $c_p=0·249$ and $C_p=6·983$ at 20°, and L. Holborn and F. Henning, for a gas with about one per cent. of oxygen :

	0°–200°	0°–400°	0°–600°	0°–800°	0°–1000°	0°–1200°	0°–1400°
Sp. ht. . . .	0·239	0·243	0·246	0·250	0·254	0·258	0·262

L. Holborn and L. Austin gave for the mean sp. ht. at constant press., 0·2419 from 20° to 440° ; 0·2464 from 20° to 630° ; and 0·2497 from 20° to 800°. J. H. Brinkworth found $c_p=0·2468$ at 10° ; 0·2471 at —78° ; and 0·2535 at —183°. P. Vieille gave 4·8 for the molar sp. ht. at constant vol. and at ordinary temp., 6·30 at 3100° ; 7·30 at 3600° ; and 8·1 at 4400° ; while M. Berthelot and P. Vieille gave

	2810°	3191°	3993°	4024°	4309°	4394°
C_v	6·67	7·93	8·43	8·39	9·85	9·60

There is thus a rapid increase in the thermal capacity of the gas, and these results were represented by $C_v=6·7+0·0016(\theta-2800°)$. J. H. Brinkworth obtained $C_v=4·922$ at 10° ; 4·910 at —78° ; and 4·914 at —183°. H. B. Dixon and co-workers gave $C_v=4·775+0·00042T_1$. S. W. Saunders gave for the best representative value, $C_p=6·41+0·000523T$. E. Mallard and H. le Chatelier, C. K. Ingold and E. H. Usherwood, E. Schreiner, and D. Clerk made some observations on this subject. For the liquid, H. Alt gave 0·430 between —208° and —196°. A. Eucken found that the mol. hts. of liquid nitrogen are $C_p=13·15$ at —208·4°, and 13·33 at —200·3°. For the ratio of the two sp. hts., S. Valentiner gave $\gamma=1·45$ at —192° ; A. Cazin, 1·41 at 15° ; O. Buckendahl, 1·405 at 0° ; G. Schweikert, 1·405 at 0° ; F. A. Schulze and A. Rathjcb, 1·412 ; H. B. Dixon and co-workers, 1·406 at 0° ; J. R. Partington and co-workers, 1·405 at 16·7° and 1·4045 at 20° ; and E. Rohlf, 1·389 at 17°. J. H. Brinkworth found 1·4054 at 10° ; 1·4103 at —78° ; and 1·4454 at —183°. W. G. Shilling gave :

$T°$ K. . . .	300°	500°	1000°	1500°	2000°	2500°	3000°
C_v . . .	4·92	4·96	5·20	5·63	6·20	6·77	6·95
C_p . . .	6·92	6·94	7·19	7·62	8·18	8·76	8·94
γ . . .	1·405	1·402	1·382	1·353	1·321	1·293	1·206

and he also gave $C_v=4·93\times10^{0·000002125T^{1·39}}$; as well as $C_v=5·014-0·0_3504T+0·0_68376T^2-0·0_91449T^3$. E. Burlot gave 1·36 at 1890°, and 1·43 at 2096°. E. Schreiner studied the mol. ht. of nitrogen. H. Buff estimated the at. ht. of tervalent nitrogen to be 7·7, and of quinquevalent nitrogen, 4·3 ; while J. Tollinger gave 4·7 for nitrogen in ammonium chloride, and 6·6 in the nitrate. G. Piccardi studied the thermal capacity of the gas.

A. Eucken found that solid nitrogen has a **transition point** at —237·5°, and melts at —209·9°. The mol. hts. of **α-nitrogen** or *nitrogen-II* at —256·5° are $C_p=3·48$, and $C_v=3·46$; and at —239·9°, $C_p=9·63$ and $C_v=9·39$. The mol. hts. of **β-nitrogen** or *nitrogen-I* are $C_p=8·84$ and $C_v=8·61$ at —236° ; and $C_p=11·08$, and $C_v=10·48$ at —212·4°. The value of C_p was calculated from that of C_v by the expression $C_p-C_v=0·0_481TC_p{}^2$—*vide supra*, the crystalline form at low temp.

The **Joule-Thomson effect** with nitrogen has been measured by J. P. Joule and W. Thomson,[10] M. Jakob, and K. Olschewsky. According to J. P. Dalton, for $\theta=0°$ and $p=$one atm.,

p . . .	5	10	15	20	25	30	35	40	45
$\delta\theta$ . . .	1·13°	2·51°	3·88°	5·25°	6·59°	7·92°	9·24°	10·48°	11·69°

The inversion temp. is 243° at 159 atm., and 163° at 30 atm. Observations were also made by H. W. Porter. W. H. Keesom calculated 331° for the inversion temp.

L. Cailletet[11] first observed the **liquefaction** of nitrogen. When the dried and purified gas was compressed at 200 atm. press., and 13° to 29°, and suddenly expanded, he observed the formation of a mist which condensed to small drops and which disappeared in about 3 seconds. This observation was confirmed by M. Berthelot; H. Erdmann also made observations on this subject. Later on, S. von Wroblewsky and K. Olschewsky cooled the gas, under 150 atm. press., to —136° by liquid ethylene; and on expanding the gas slowly, liquefaction occurred. The liquid persisted but a few seconds. K. Olschewsky improved the process. J. P. Kuenen, and J. H. Simons studied the liquefaction of mixtures with oxygen.

S. von Wroblewsky found that at the temp. of liquid oxygen, —186°, compressed nitrogen furnishes large snow-like crystals of the solid; K. Olschewsky could not confirm this observation, but he obtained a crystalline mass of nitrogen by cooling the liquid with evaporating liquid hydrogen. W. Wahl obtained good crystal growths by cooling purified liquid nitrogen. The crystals are dark in all positions between crossed nicols, and they are therefore isotropic; the crystals belong to the cubic system. This result is in harmony with the crystal symmetry of the other members of this family, because although these elements exist in several polymorphic modifications, the forms of phosphorus and arsenic which are stable at the lowest temps. belong to the cubic system, it is also probable of yellow antimony. D. Vorländer and W. H. Keesom did not agree—*vide supra*. The **critical temperature** obtained by K. Olschewsky is —146°, and the **critical pressure,** 33 atm.; J. Dewar obtained respectively —146° and 35°; S. von Wroblewsky, —146·0° to —146·5°, and 33 to 35 atm., and E. Mathias and C. A. Crommelin, —147·13° and 33·49 atm.; and E. Cardoso, —144·6° and 33·65 atm. The subject was studied by W. Herz. E. Sarrau gave 0·004603 for the **critical volume;** and L. Cailletet and P. Hautefeuille, 0·37 for the **critical density;** E. Mathias and C. A. Crommelin, 0·31096. For the latter, S. von Wroblewsky gave 0·44; J. Dewar, 0·3269; E. Mathias and co-workers, 0·31096; and H. Happel, 0·315. J. A. Muller gave 1·285 for the degree of polymerization in the critical state. W. Herz examined the relations of the critical constants. S. F. Pickering gave for the best representative values T_c=126·0° K.; p_c=33·5 atm.; and D_c=0·3110. S. von Wroblewsky found the **vapour pressure** of the liquid to be 32·3 atm. at —146·6°; 20·7 atm. at —153·7°; 1·0 atm. at —193·0°; and 0·105 atm. at —202·0°. E. C. C. Baly found for the vap. press. of chemical and atm. nitrogen:

T° K.	77°	80°	85°	90°	91°
Chem. N	717·0	1013·0	1705·5	2686·0	2916·5
Atm. N	716·0	995·0	1646·0	2581·0	2812·0

C. A. Crommelin represented the vap. press. of liquid nitrogen between —191·88° and —148·85° from p=1·4727 to 20·304 atm., by the expression $\log p=5{\cdot}76381-853{\cdot}522T^{-1}+54372{\cdot}3T^{-2}-1783500T^{-3}$. The vap. press. at the m.p. is 93·5 mm. Observations on the vap. press. of nitrogen up to about one atm. have also been made by K. T. Fischer and H. Alt, G. Holst and L. Hamburger, H. K. Onnes and co-workers, E. C. C. Baly, F. Henning and W. Heuse, P. G. Cath, and H. von Siemens. Higher vap. press. were measured by K. Olschewsky, and C. A. Crommelin, while F. Porter and J. H. Perry gave:

	—182·88°	—177·56°	—174·36°	—166·03°	—159·40°	—154·06°	—151·53°
p atm.	3·631	5·583	7·056	12·193	17·85	23·57	26·75

and these results are represented by $\log_{10} p=-302{\cdot}34T^{-1}+3{\cdot}94127-0{\cdot}00274T+0{\cdot}0_5 1116(T-100{\cdot}5)^3$; and E. Mathias and co-workers gave $\log p=-510{\cdot}64T^{-1}+12{\cdot}831-0{\cdot}12696T+0{\cdot}0008302T^2-0{\cdot}0_5 19975T^3$. H. von Siemens represented the vap. press. of liquid nitrogen by $\log p=-323{\cdot}5T^{-1}+1{\cdot}75\log T-0{\cdot}01292T+5{\cdot}0527$; and of solid nitrogen by $\log p=-345{\cdot}6T^{-1}+1{\cdot}75\log T-0{\cdot}00696T-4{\cdot}7306$. F. A. Henglein gave $\log p=4{\cdot}6222\{(77{\cdot}24/T)^{0{\cdot}89106}+1)\}$—with p in atm. F. Porter and J. H. Perry gave $\log_{10} p=-302{\cdot}34T^{-1}+3{\cdot}94127-0{\cdot}00274T$

$+1{\cdot}116\times10^{-8}(T-100{\cdot}5)^3$. F. Henning gave for the liquid, $\log p=-313{\cdot}694T^{-1}+1{\cdot}75\log T-0{\cdot}011109636T+4{\cdot}487879$, or $\log p=-360{\cdot}500T^{-1}+7{\cdot}679324$; and B. F. Dodge and H. N. Davis, for p atm., $\log_{10}p=-316{\cdot}824T^{-1}+4{\cdot}47582-0{\cdot}0071701T+0{\cdot}0_4294T^2$; or $\log_{10}p=-304{\cdot}494T^{-1}+3{\cdot}93352$. For the vap. press. of mixtures of oxygen and nitrogen, *vide* **1.** 13, 26. V. Fischer studied the vap. press. of mixtures of nitrogen and argon; V. Fischer, and B. F. Dodge and A. K. Dunbar, the vap. press. of mixtures of nitrogen and oxygen—*vide* **1.** 13, 26; and I. R. McHaffie, and E. P. Bartlett, the vap. press. of water in nitrogen compressed over that liquid. V. Kirejeff discussed what he called the cohesive press. of nitrogen. S. von Wroblewsky gave for the **boiling point** of liquid nitrogen —193° at 740 mm.; —201° at 120 mm.; —202·5° at 70 mm.; —204° at 60 mm.; and —206° at 42 mm. J. Dewar made observations on the b.p. of liquid nitrogen. K. Olschewsky gave —194·4° at 760 mm.; L. Grunmach, —195·9° at 749·1 mm.; A. Stock and C. Nielson, —195·35° at 763 mm.; F. Henning and W. Heuse, —195·81° at 760 mm.; E. Mathias and C. A. Crommelin, —195·78°; B. F. Dodge and H. M. Davis, —195·80°; F. Henning, —195·78° to —195·81°; and K. E. Fischer and H. Alt, —195·67° at 760 mm., or —196·176° at 714·5° mm., and —210·52° for the **melting point** at 84 mm. press.; J. Dewar, —210·5°; H. Erdmann, —211°; W. Guertler and M. Pirani, —210°; F. Henning, —209·882°; and A. Eucken, —209·9°. S. von Wroblewsky gave —199° to —203° for the f.p. of the liquid, and K. Olschewsky, —214° at 60 mm. press. W. Herz found that in the equation $\theta_1/\theta_2=T_1/T_2+c(\theta_1-T_1)$, the constant c varies from 0·0007979 to 0·0008695; and θ_1 and θ_2 denote the b.p. of two liquids at a given press., and T_1 and T_2 the b.p. of the same liquids at another press. E. Mathias and C. A. Crommelin gave for the **triple point,** —209·86° and —0·64 atm. press.; and F. Henning, —209·88°, and 92·89 mm. press. For the **heat of vaporization,** J. S. Shearer gave 0·698 Cal. per gram-atom, and 49·83 cals. per gram. D. L. Hammick gave 50·04 cals.; A. Eucken, 1350 cals. per mol; H. Alt gave 1336 cals. per mol, and 47·65 cals. per gram, and he represented the former as a linear function of the temp., $L=1{\cdot}073-0{\cdot}2428\theta$. L. I. Dana gave for the latent heat of vaporization, L cals. per gram for mixtures of nitrogen with p per cent. of oxygen:

p . .	0	10	20	40	60	80	90	100
L . .	47·74	48·37	48·98	50·07	50·83	51·23	51·18	51·01

N. de Kolossowsky studied the relation between the thermal expansion and the heat of vaporization; P Walden, the relation between the capillary constants and the heat of evaporation; and E. Mathias and co-workers, the relation between the latent heat of vaporization and the difference of the sp. hts. of sat. vapour and liquid; and gave $L^2=89{\cdot}9621(T_c-T)-1{\cdot}47242(T_c-T)^2+0{\cdot}003321T^2-0{\cdot}0_43219T^3$, where T_c denotes the critical temp. T. Estreicher found the mol. lowering of the f.p. of nitrogen to be 5·39, and hence computed the **heat of fusion** to be 12·82 Cals. or 53·47 joules. A. Eucken found the heat of fusion of β-nitrogen to be 168·7 cals. per mol; and the **heat of transformation** from α- to β-nitrogen to be 53·8 cals. per mol. E. E. Walker studied the degree of association. From the work of I. Langmuir, A. Eucken, and E. J. B. Willey and E. K. Rideal, the **heat of dissociation** of nitrogen into atoms: $N_2=2N$ is greater than 190,000 cals. and probably of the order 300,000–400,000 cals. per mol. M. Saha believed this value to be much too high. W. Kuhn gave 140 Cals., H. D. Smyth, 145 Cals. K. T. Compton did not succeed in dissociating the molecules thermally—*vide infra,* ionizing potential. R. T. Birge and H. Sponer calculated from the band spectra of N_2, 11·9 volts or 274,000 cals., or 11·4 volts or 263,000 cals. from active nitrogen; and for the $N_2{}^+$-molecule, 9·1 volts or 210,000 cals. from the band spectra. J. C. Thomlinson discussed the heats of formation of various compounds and deduced what he called the **thermochemical equivalent** of nitrogen. K. Bennewitz and F. Simon discussed the energy of the nitrogen molecule. G. N. Lewis and co-workers gave 22·8 for the **entropy** of $\frac{1}{2}N_2$, and also 33·57 for N at 25°; and

B. Bruzs gave 19·0 for the entropy of nitrogen at the m.p., and at 25°. H. C. Urey gave for N_2, 45·59; and E. D. Eastman, 45·6. W. H. Rodebush and co-workers constructed some temp.-entropy diagrams, at 25° and one atm. press. E. Kordes calculated $1·35Q_{\text{cals.}}/T$ for N, 2·7 for N_2, and 5·4 for N_4.

Measurements have been made of the **index of refraction** of nitrogen ranging from J. Koch's[12] $\mu=0·0_33261$ for $\lambda=0·2379\mu$, $\mu=0·0_330937$ for $\lambda=03342\mu$, C. and M. Cuthbertson's $\mu=0·0_33012$ for $\lambda=0·4861\mu$, to H. C. Rentschler's $\mu=0·0_32998$ for $\lambda=0·5461\mu$; and K. Scheel's $\mu=0·0_32945$ for $\lambda=0·7056\mu$. Observations were also made by W. Ramsay and M. W. Travers, M. Croullebois, J. H. Gladstone, E. Stoll, L. Lorenz, and E. Mascart. E. W. Cheney gave $1·0_32985$ for $\lambda=5852$ A.; $1·0_32977$ for $\lambda=6143$ A.; and $1·0_32969$ for $\lambda=6678$ A. C. and M. Cuthbertson gave $\mu=5·0345\times10^{27}/(17095\times10^{27}-n^2)$; and J. Koch preferred the formula:

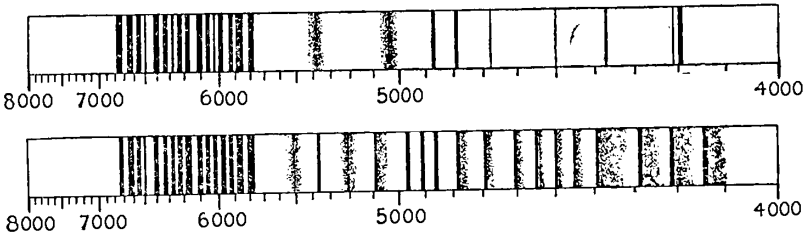
$$\frac{3}{2}\cdot\frac{\mu^2-1}{\mu_2+2}=\frac{3953450\times10^{-8}}{152·294-\lambda^{-2}\times10^{-8}}+\frac{837340\times10^{-8}}{250·65+\lambda^{-2}\times10^{-8}}$$

on the assumption that two kinds of electrons are concerned in the phenomenon. G. D. Liveing and J. Dewar found the index of refraction of liquid nitrogen (containing about 5 per cent. of oxygen) to be 1·2053. E. Gerold studied the optical constants of gaseous nitrogen at its b.p., and found for the gas at 77·97° K. and 752·32 mm. $\mu=1·0010779$ for $\lambda=643·9$; 1·0010847 for $\lambda=546·1$; and 1·0011007, for $\lambda=436·8$; and for the liquid at 77·12° K., and 745·12 mm., $\mu=1·19844$ for $\lambda=656·3$; 1·19876 for $\lambda=579·1$; 1·19918 for $\lambda=546·1$; 1·20042 for $\lambda=435·8$; and 1·20258 for $\lambda=404·7$. J. Cabannes and J. Granier observed the polarization of light laterally diffused in nitrogen. J. H. Gladstone gave for the **specific refractory power,** $(\mu-1)/D=0·293-0·379$; and A. Schrauf, $(\mu^2-1)/D=0·000596$. The subject was studied by C. P. Smyth. J. E. Calthorp, and W. Herz examined the relation between the at. vol. and the index of refraction. C. E. Guye and R. Rudy, and T. H. Havelock studied the electromagnetic rotatory power of nitrogen. J. H. Gladstone gave for the **refraction equivalent,** 4·1–5·1; and R. Löwenherz found for the **atomic refraction** of nitrogen in organic amines and nitrates, 2·870 with the $(\mu^2-1)/(\mu^2+2)$ formula, and 5·38 with the $(\mu-1)$-formula; and for gaseous ter- or quinque-valent nitrogen, both formulæ give too low values. J. W. Brühl calculated 2·21 for the atomic refraction of gaseous nitrogen with the μ^2-formula. G. D. Liveing and J. Dewar gave 8·405 for the mol. refractory power; and 1·205 for D-light, of liquid nitrogen at −190°. R. Frazer observed no change in the refractive index of nitrogen when subjected to magnetic field of 184 gauss. A. Glaser found that nitrogen is oriented in a magnetic field, and hence the atoms and molecules react to light in a manner independent of their orientation. K. von Auwers and co-workers studied the optical properties of nitrogen compounds; and W. Strecker and R. Spitaler, the relation between the index of refraction and structure of organic compounds.

The **electromagnetic rotation of the plane of polarized light** in nitrogen was measured by H. Becquerel,[13] and A. Kundt and W. C. Röntgen. According to L. H. Siertsema, the value for wave-lengths, λ, between $0·423\mu$ and $0·684\mu$, at 14°, and 100 kgrms. per sq. mm. press., is $\omega=0·0001712\lambda^{-1}+0·00004519\lambda^{\ 3}$. C. V. Raman and K. S. Krishnan calculated $0·04\times13^{-10}$ for their constant at 20°. E. Stoll gave for the **dispersion of light** of wave-length $\lambda=4388$ to 9224 A., in nitrogen, $(\mu-1)10^7=2977·27+22·65\lambda^{-2}$, when it is expressed in μ. The **scattering of light** and polarization in nitrogen was studied by Lord Rayleigh. K. R. Ramanathan and N. G. Srinvasan found that the depolarization of light scattered by nitrogen supports the view that the configuration of the outer electrons is like that of the electrons of carbon monoxide.

Quite a number of different spectra of nitrogen have been described. There are the line spectrum, five-band spectra, one of nitrogen at the anode, one of nitrogen at the cathode, one attributed to the oxygen compounds of nitrogen, and one to ammonia. According to J. Trowbridge and T. W. Richards,[14] the so-called channelled spectrum is always obtained by a continuous discharge with no spark-gap or brush discharge in the circuit—the glow in the capillary and about the electrodes has a delicate pink colour. When an air-gap over which the battery discharges in a brush is introduced into the circuit, the glow becomes more violet, and the red band decreases in intensity, and this the more the larger the size of the air-gap—finally the red bands almost wholly disappear and the green and blue bands impart a blue glow to the gas in the capillary. If a condenser is introduced in the circuit, the blue colour changes to a rich bluish-green, and if the condenser discharge is damped by a suitable resistance, the channelled spectrum reappears. The **line spectrum** of nitrogen is produced when a jar-discharge passes through the gas, and when the spectra of metals are examined by allowing the jar-discharge to pass between the metal electrodes in air. The main lines in the green spectrum of nitrogen are shown in Fig. 5. Observations were made by D. Brewster, W. A. Miller, A. J. Angström, D. Alter, J. Plücker, H. W. Dove, V. S. M. van der Willigen, E. Robiquet, G. Kirchhoff, G. G. Stokes, H. C. Dibbits, C. Fievez, A. Ditte, H. Deslandres, G. Séguy, R. Nasini and F. Anderlini, A. Mitscherlich, J. Chautard, W. Huggins, H. F. Brasack, A. Fowler and L. J. Freeman, and A. Schimkoff. J. Formanek gave for the more important lines in the spectrum of nitrogen 5942, and 5933 in the orange-yellow; 5679, 5675, and 5667 in the yellowish-green; 5542, 5535, 5531, 5496, 5480, 5046, 5026, 5017, 5011, 5006, 5003, 4994, and 4988 in the green; 4804, 4789, 4780, 4641, 4629, 4606, and 4601 in the blue; 4446 and 4348 in the indigo; and 4237, 4229, and 3995 in the violet. M. Curie studied the spark spectrum of liquid nitrogen; D. A. Keys and M. S. Home, the striated discharge in mixtures of hydrogen and nitrogen; and B. Trumpy, the breadths and intensities of the lines.

The **band spectrum** of nitrogen in a vacuum tube was observed by J. Plücker, and in the brush discharge of an ordinary electrical machine, by V. S. M. van der Willigen. It is illustrated by Fig. 6. The spectrum was studied by J. Plücker and J. W. Hittorf, H. Nagaoka, J. C. Slater, R. T. Birge and J. J. Hopfield, T. R. Merton and J. G. Pilley, R. Sewig, H. Kirschbaum, L. and E. Bloch, W. Steubing and M. Toussaint, P. Lindau, M. Duffieux, M. Fassbender, H. Sponer, R. T. Birge, G. H. Diecke, R. Mecke, R. S. Mulliken, M. Guillery, E. E. Witmer, A. J. Angström and R. Thalén, M. Hamy, and L. de Boisbaudran. The bands in the red and yellow appear different from those in the blue and violet. Hence, J. Plücker and J. W. Hittorf said that two spectra are really superposed and are really produced by two different sets of mols. By increasing the diameter of the capillary part they obtained a tube which showed only the red and yellow bands; and added:



FIGS. 5 and 6.—The Band, and the Green Spectra of Nitrogen.

> We succeeded in constructing a tube which, when the direct discharge was sent through it, became incandescent with the most brilliant gold-coloured light, which might easily be confounded with the light of highly-ignited vapours of sodium; but with the intercalated jar, the light of the incandescent gas within the same tube had a fine bluish-violet colour. The yellow light when analyzed by the prism gave a beautiful spectrum of shaded bands, extending with decreasing intensity to the blue, the channelled spaces being scarcely

perceptible. The bluish light when examined was resolved by the prism into channelled spaces, extending towards the red; while the former bands almost entirely disappeared. We may transform each colour and its corresponding spectrum into the other *ad libitum.*

G. Salet showed that sodium may be heated in the tube containing the nitrogen without changing the spectrum, and hence inferred that the spectrum is really due to nitrogen and not to an oxide. A. J. Angström and R. Thalén considered that the band spectrum is due to an oxide because with a discharge in air showing the band spectrum, the formation of nitrogen oxide can be demonstrated. A. Schuster, however, considered G. Salet's experiment decisive. The subject has been examined by A. Secchi, H. C. Vogel, A. Schuster, A. Wüllner, A. Cazin, W. Crookes, E. Goldstein, B. Hasselberg, G. D. Liveing and J. Dewar, C. P. Smyth, H. Deslandres, A. T. Sundell, J. S. Ames, E. Warburg, L. Zehnder, J. Trowbridge and T. W. Richards, A. Kalähne, E. S. Ferry, G. A. Hemsalech, G. Berndt, C. Cuthbertson, H. Crew and J. C. Baker, C. C. Hutchins, P. Lewis and A. S. King, A. Hagenbach and H. Konen, J. Stark, P. G. Nutting, A. Hagenbach, J. Schniederjost, E. E. Lawton, R. von der Helm, F. Himstedt and H. von Dechend, etc. M. Toussaint studied the effect of argon, and of iodine on the band spectrum of nitrogen; and W. Schütz, the effect of nitrogen on the spectrum of sodium. M. Duffieux studied the mass of the particles emitting the band spectrum of nitrogen.

J. Plücker and J. W. Hittorf also showed that with a condensed discharge, the vacuum tube glows with a white light. This gives a line spectrum which is identical with that of the spark discharge, but has no relation with the band spectrum just indicated. These observations were confirmed by A. Wüllner, E. Reitlinger and M. Kuhn, O. Schenk, and L. de Boisbaudran. The line spectrum has been also examined by A. Secchi, H. C. Vogel, G. Salet, A. Cazin, O. Neovius, J. Trowbridge and T. W. Richards, A. Schultz, W. Wien, H. Deslandres, H. Moissan and H. Deslandres, G. A. Hemsalech, F. Exner and E. Haschek, G. Berndt, P. Hermesdorf, J. Stark, P. W. Merrill and co-workers, P. G. Nutting, and A. Hagenbach and H. Konen. M. Curie studied the spark discharge in liquid nitrogen. G. M. J. McKay observed no evidence of spectral lines from nitrogen heated to 3200° K., and he attributed the spectrum obtained by A. S. King, and G. A. Hemsalech from the heated gas to a chemical action of some kind. The **arc spectrum** has been examined by B. Walter, A. Hagenbach, A. H. Pfund, K. T. Crompton and O. S. Duffendack, R. A. Wolfe and O. S. Duffendack, A. S. King, T. R. Merton and J. G. Pilley, K. T. Compton, and C. T. Kwei; the **ultra-red spectrum,** by E. R. Drew, J. C. McLennan and co-workers, A. H. Pfund, J. W. Ellis, W. W. Coblentz, E. O. Salant, and R. von der Helm; the **ultra-violet spectrum,** by H. Deslandres, H. Kreusler, G. Berndt, L. Ciechomsky, P. Baccei, F. Exner and E. Haschek, J. J. Hopfield and S. W. Leifson, S. W. Leifson, I. S. Bowen and S. B. Ingram, I. S. Bowen and R. A. Millikan, O. Oldenburg, A. W. Wright and E. S. Downs, V. Schumann, A. Dauvillier, and J. Schneiderjost; the **electrodeless tube spectrum,** by P. D. Foote and A. E. Ruark, and P. Lewis; the **flame spectrum,** by J. Schneiderjost, and C. de Watteville; the **canal ray spectrum,** by A. Schultz, E. Goldstein, J. Stark and co-workers, W. Hermann, E. E. Lawton, R. Pohl, and V. Berglund; and the **absorption spectrum,** by E. Luck, A. Kundt, P. M. Garibaldi, L. Cailletet, J. N. Lockyer, J. Moser, J. L. Schönn, F. Holweck, B. Hasselberg, J. L. Soret, W. J. Russell and W. Lapraik, W. N. Hartley, R. T. Birge, P. Hautefeuille and J. Chappius, G. H. Dieke, G. D. Liveing and J. Dewar, and P. Baccei. F. C. Brickwedde and W. A. MacNair found no absorption with liquid nitrogen between wave-lengths 2000 A. and 6500 A. M. Fassbender studied the **negative band-spectrum**; V. S. M. van der Willigen found that the **spectrum of the negative glow** in a nitrogen tube is not usually shown in other parts of the tube. It was mapped by A. J. Angström and R. Thalén. It is a channelled spectrum fading away towards the blue. The bands partially overlap some of the bands of the spectrum of the positive discharge. The bands of the spectrum of the negative glow belong to a spectrum distinct from the ordinary spectrum of the positive discharge although traces of the former may occur in the latter. If the press. is much reduced, the negative glow gradually extends throughout the whole tube. This subject has been examined by F. Brasack, A. Schultz, A. Schuster, P. Lewis, and H. Deslandres, and the spectrum of the after-glow and the fluorescence in a vacuum tube, by P. Lewis, O. Oldenberg, and K. von Mosengeil. O. Oldenberg studied the fluorescence of nitrogen in the ultra-violet; J. C. McLennan and co-workers, G. Cario, and D. A. Keys, the phosphorescence spectrum of solid nitrogen bombarded by electrons—the 5577 line is due to oxygen, *vide supra*, air; B. Reismann, and L. Vegard, the cathode ray spectrum of nitrogen in a vacuum tube. O. Oldenberg found that the fluorescence produced in nitrogen by short-wave, ultra-violet light has a spectrum showing bands due to neutral and ionized molecules. H. O. Kneser studied the excitation of the bands by electron collisions.

Lord Rayleigh, R. C. Johnson, and W. Steubing and M. Toussaint studied the effect of the *inert gases* on the band spectrum of nitrogen. A. Wüllner described the changes which occur in the spectrum of nitrogen as the *pressure* in the tube is gradually increased. S. Datta studied the effect of bromine on the spectrum of nitrogen; W. H. B. Cameron, the effect of neon; D. A. Keys and M. S. Home, the effect of hydrogen; and C. Füchtbauer and G. Joos, the broadening of the spectral lines by other gases. The effect of press. has been also examined by E. Villari, E. Goldstein, J. Huddleston, A. Cazin, W. Crookes, T. R. Merton, and A. Zehden; and the effect of a low *temperature*, by K. R. Koch, J. C. McLennan and G. M. Shrum, M. Cantone, A. Hagenbach, and J. P. Donaghey. According to H. Erdmann and co-workers, the reddish-violet colour of the ordinary discharge tube, showing the band spectrum, becomes greenish-yellow when cooled with liquid nitrogen, and then it shows the line spectrum. L. Vegard and co-workers, and J. C. McLennan and co-workers, studied the spectrum of the light emitted by bombarding solid nitrogen, and mixtures of nitrogen and neon, with high velocity cathode rays, at the temp. of liquid helium, D. C. Duncan, and H. O. Kneser, the spectrum produced by electronic impacts; H. Kerschbaum, the duration of the light emitted by arc and spark. The effect of a *magnetic field*—the *Zeeman effect*—was examined by W. Schütz, J. Chautard, H. Krefft, G. Berndt, W. Wien, L. Grebe and A. Bachem, J. E. Purvis, W. Steubing, and N. Vaccaro; of an *electric field*, by U. Yoshida, and S. Datta; the *Doppler effect*, by J. Stark, H. Rau, H. Krefft, and W. Hermann; J. A. Schwindler, the effect of the *potential* and *frequency* of the spark; and L. Grebe and A. Bachem, the *gravitational displacement* of the $\lambda=3883$ A. line of the solar spectrum. The spectra of the *nitrogen oxy-compounds* have been described by G. L. Ciamician, G. Scheibe, E. Demarçay, L. Bell, W. N. Hartley, P. Lewis, H. O. Kneser, A. Dufour, and E. Warburg and G. Leithäuser; and the spectrum of *ammonia*, by A. Schuster, K. B. Hofmann, J. L. Schönn, L. de Boisbaudran, H. O. Kneser, G. Magnanini, L. Zehnder, R. Mecke and P. Lindau, W. N. Hartley, P. Lewis, J. Trowbridge, and W. H. Bair; of *amines*, by H. Ley and F. Volbert, and G. Scheibe; while W. W. Coblentz, E. O. Salant, J. W. Ellis, E. Hulthèn and S. Nakamura, W. Jevons, K. von Auwers and R. Kraul studied the spectrochemistry of the nitrogen compounds.

Regularities in the spectral lines have been discussed by A. Kratzer, R. A. Millikan and I. S. Bowen, I. S. Bowen, R. Rudy, B. Rosen, H. Sponer, C. C. Kiess, F. Croze, F. Croze and J. Gilles, L. de Boisbaudran, G. J. Stoney, D. Gernez, J. Stark and O. Hardtke, H. Deslandres, and H. Deslandres and A. Kannapell. J. J. Hopfield, A. Fowler, S. Datta, identified **series spectra.** This makes it appear as if the ordinary line spectrum is the spark spectrum of N^+; while A. Fowler has suggested that the so-called enhanced lines, obtained by using a powerful stimulus, may represent a second stage in the ionization. E. Hulthèn and G. Johansson, K. Beckert and M. A. Catalan, C. C. Kiess,

M. Holweck, and P. Lindau studied the structure of the nitrogen bands. E. Condon, and R. Mecke discussed the distribution of energy in the band spectrum. M. Duffieux estimated the masses of the particles that produce the nitrogen spectrum.

F. Holweck,[15] and A. Dauvillier studied the K-series of the **X-ray spectrum**; and C. G. Barkla, the J-series. The **scattering of X-rays** in nitrogen has been studied by J. A. Crowther, J. S. Townsend, and C. W. Hewlett; the absorption of X-rays, by T. E. Aurén, and F. Holweck, and the diffraction of X-rays in liquid nitrogen, by W. H. Keesom and J. de Smedt; and J. M. Nuttall and E. J. Williams, the ranges of the β-rays in nitrogen; G. P. Harnwell, H. K. Erikson, H. Kallmann and M. A. Bredig, J. W. Broxon, S. P. McCallum and C. M. Focken, W. W. Merrymon, and I. Langmuir and H. A. Jones investigated the **ionization** of nitrogen; T. L. R. Ayres, and K. T. Compton and C. C. van Voorhis, the ionization by collision; P. M. S. Blackett, W. P. Jesse, R. W. Gurney, ionization by α-particles, and by slow electrons; H. Sponer and co-workers, the **heat of ionization,** $N_2 \rightarrow N^{\cdot}_2$. H. D. Smyth, A. L. Hughes, K. T. Compton and C. C. van Voorhis, and T. R. Hogness and E. G. Lunn, studied the ionization of nitrogen by electronic impact, and the results show that the ordinary ionizing potential at 16·9 volts corresponds with the production of singly charged mol. ions, $N^{\cdot}_2$; and singly and doubly charged atomic ions, $N^{\cdot\cdot}$, $N^{\cdot}$, at 27·7 volts. T. R. Hogness and E. G. Lunn, and R. T. Birge discussed the energy levels of the nitrogen mol. T. L. R. Ayres studied the collision frequency of electrons and molecules; and V. H. Bailey, the attachment of electrons to the molecules of nitrogen. The **velocity of the ions** in an electric field with a potential difference of one volt per cm. was found by J. Franck to be 1·27 cms. per sec. for the positive ions and 1·84 to 120·4 cms. per sec. for the negative ions from polonium at 15° and 760 mm. W. B. Haines obtained 370–500 cms. per sec.; H. B. Wahlin, 18,000 cms. per sec.; and L. B. Loeb, about 10,000 cms. per sec. L. Meitner and K. Freitag studied the tracks of the α-particles in nitrogen; J. M. Nuttall and E. J. Williams, the tracks and ranges of the β-rays in nitrogen; P. Auger, the photo-electrons; O. Laporte, the mobilities of ions in nitrogen; and M. C. Johnson, the velocities of the ions in stellar atmospheres under the influence of radiation pressure. For the **diffusion coefficient of ions** in nitrogen E. Salles obtained 0·0295 sq. cm. per sec. for the positive ions, and 0·041 for the negative ions. H. F. Mayer, and R. B. Brode studied the absorption of slow moving electrons by nitrogen mols. S. P. McCallum and C. M. Focken measured the rate of increase of current due to ionization when the electrons are produced by a heated filament and by ultra-violet light; and they compared the effect of ionization by collision with that due to radiation. J. S. Townsend and V. A. Bailey estimated that when an electron moving with a velocity of the order of 10^8 cms. per sec. collides with a mol. of nitrogen, it loses more than 1 per cent. of its energy. C. Ramsauer studied the effective cross-sectional area in collision between the mols. of nitrogen and electrons. R. B. Brode studied the mean free path of the electrons; E. Brüche, the area offered by nitrogen molecules to slow electrons; W. Harries, the loss of energy by the collision of slow electrons with nitrogen molecules; and G. P. Harnwell, inelastic collisions in ionized mixtures of nitrogen and the rare gases.

O. S. Duffendack and D. C. Duncan studied the excitation of the spectra of nitrogen by electronic impacts; and V. Kondratéeff found that a voltage of 32 ± 2 is necessary to make the band spectrum of nitrogen appear, although atomic lines made their appearance first. The nitrogen molecule can break down in one action into excited atoms $N_2 \rightarrow N' + N'$, or $N_2 = N' + N^{\cdot} + \Theta$. B. Davis and F. S. Goucher showed that the ionization at about 7·5 volts is not really the **ionizing potential,** but rather represents the least energy an electron must have in order that it may excite radiation by the bombarded mol.; they gave about 18 volts for the ionizing potential. H. D. Smyth obtained a similar result, and

E. Brandt obtained 17·75 volts, and higher ionization stages at 25·41 volts and 30·72 volts—C. B. Bazzoni and A. T. Waldie confirmed these results—B. Davis gave 17 and 29·9 volts; G. B. Kistiakowsky, 17 volts; G. Stead and B. S. Gossling, 17·2 volts; and R. A. Morton and R. W. Riding, 17·01 volts. L. and E. Bloch found that the negative band spectrum of nitrogen has an ionizing potential of 21·5 volts, and the positive band spectrum of 12 volts. E. E. Witmer gave 18 volts for the critical potential of the negative band spectrum of nitrogen. G. Kistiakowsky found ionization potentials for nitrogen on an iron catalyst at 11·1, 13·0, 16·0, and 17·1 volts. K. T. Compton, A. S. Levesley, and A. L. Hughes and A. A. Dixon made observations on this subject. A. E. Ruark and co-workers gave 16·9 volts for the ionizing potential of nitrogen, and 8·18 volts for the inelastic collision potential; O. S. Duffendack gave 16·2 volts; C. A. Mackay, 16·3 volts. P. E. Boucher gave for the ionizing potential 15·8 volts; for the **resonance potential,** 8·4 volts; and for the potentials at which radiation is prominent, 8·4–15·8 volts. F. L. Mohler and P. D. Foote gave 8·18 volts for the resonance potential and 16·9 volts for the ionization potential. The resonance potential corresponds with the nitrogen doublet at λ=1492·2 A., and 1494·8 A., whilst the ionizing potential corresponds with the first term of the spectral series converging at λ=730 A. P. E. Boucher, R. Rudy, B. Rosen, H. E. Krefft, J. Franck, and C. G. Found made observations on this subject. N. Perrakis worked out a relation between the ionizing potential and the critical constants. B. Davis studied the relation between the critical potentials and the indices of refraction.

The **discharge tension** of the current required for spherical electrodes was found by A. Orgler[16] with nitrogen at different press., p, and with spark gaps 0·50 cm. and 0·10 cm., to be

p . . .	750	650	450	250	100	60	40 mm.
Kilovolts (0·5) .	18·13	16·20	12·08	7·617	3·840	2·691	2·010
Kilovolts (0·1) .	4·890	4·398	3·366	2·235	1·218	—	—

H. Kerschbaum studied the duration of luminous cathode rays in nitrogen. Observations were also made by R. J. Strutt, W. Wien, and H. E. Hurst. Observations on the point discharge were made by E. Warburg and F. R. Gorton. M. Pirani examined the effects of minute traces of impurity on the point discharge in nitrogen; K. G. Emeléus, the distribution of the potential in the glow discharge in nitrogen; T. Terada and U. Nakaya, the structure and form of the sparks; C. Eckart and co-workers, the low-voltage arc oscilliations; and A. Günther-Schulze, and O. W. Richardson and R. Chaudhuri studied the potential gradient. According to J. Franck and G. Hertz, an electron formed in the neighbourhood of a point cathode in a pure gas can lead to a strong ionization, and consequent variation in the current, which, however, is irregular in occurrence, owing to the infrequency of the phenomenon. On the other hand, the presence of minute amounts of electronegative substances, such as oxygen, oxides of nitrogen, or water, causes an increase in the current, owing to the production of electrons at the cathode. Such a gaseous mixture, however, does not behave in a stable manner, the phenomena being complicated by the occurrence of slow chemical changes, which cause gradual alteration in the strength of the current, in accordance with the nature of the chemical processes. With a pure gas, the current rises initially, owing to the liberation of inherent impurities by the heat, but falls when the maximum of impurity has been passed. In an impure gas, on the other hand, more strongly electronegative products (such as nitric oxide) may be readily formed, thus causing a decrease in the current, which subsequently rises after partial or complete absorption of the impurities by the electrodes. M. Pirani found that the maximum current strength depends on the oxygen content. The time-current curves for mixtures containing oxygen, in contrast to those for pure nitrogen, exhibit a steep rise after a time. Obviously, the oxygen is gradually consumed, possibly by formation of nitric oxide, which is removed by the molybdenum or other oxidizable part of the apparatus. The removal is not, however, quantitative, and there remain minute traces of oxygen which raise the current strength above the normal value. The mixture in which the greatest rise was observed contained about 5×10^{-4} per cent. The appearance of the point discharge is more considerably modified by water vap. than by oxygen. The time-current curves, in contrast to those of mixtures containing oxygen, exhibit a definite and less defined minimum which gradually disappears with increasing water-vapour content, and, in particular, show a gradually rising branch, the current values for which with mixtures poor in aq. vap. lie above those for pure nitrogen, and appear to lead asymptotically to a final value. The processes on which these curves depend are obviously very complicated, owing to the dissociation of water vapour. With slight modifications, the experiments can be extended to the rare gases; the sensitiveness is greater in these cases, but the phenomena are generally similar. The presence of hydrogen in nitrogen to the extent of 0·1 per cent. or more can be detected with certainty by means of the time-current curves, but the slight elasticity of the hydrogen molecules renders the method less sensitive. O. Hammershaimb and P. Mercier, and R. H. George and K. A. Oplinger studied the sparking potential of nitrogen; and H. Stücklein, the effect of water on the sparking potential. W. Clarkson studied the flashing of argon-nitrogen discharge tubes; H. Fischer, the discharge with Tesla currents. The potential difference of the cathode for the glow discharge with different metals in nitrogen was measured by K. Rottgardt, R. Seeliger, O. S. Duffendack, R. Holm, W. Heuse, E. Warburg, and C. A. Skinner. P. D. Foote and A. E. Ruark studied the electrodeless discharge in nitrogen. G. Holst, and E. Blechsmidt studied cathodic disintegration in nitrogen.

The **dielectric constant** of nitrogen at one atm. press., and 0°, was found by H. Rohmann[17] to be 1·000606; E. Bodareu gave 1·000587 at ordinary press., and for press. at which the density is D, $(K-1)10^7=1954(K+2)D$; and K. Tangl gave for 20°, 1·00581 at one atm. press.; 1·01086 at 20 atm.; and 1·05498 at 100 atm.; and E. C. Fritts, 1·000555. C. T. Zahn found the dielectric constant, ϵ, of nitrogen to be $(\epsilon-1)10^6=1898$ at $-88·9°$; 792 at $-75·2°$; 581 at 0°; and 283 at 289·1°; and the results can be represented by P. Debye's expression $(\epsilon-1)^vT=0·000580T$, where v is the sp. vol. per c.c. of an ideal gas at n.p. θ. L. Ebert and W. H. Keesom gave 1·472 at $-209·1°$, and 1·440 at $-196·5°$ for liquid nitrogen; and 1·45 to 1·46 for solid nitrogen at $-213°$. W. Herz, K. Wolf, and G. L. Addenbrooke studied the connection between the dielectric constant and other physical properties. J. H. Jones discussed the quantum theory of dielectrics; and G. Jung, the orientation of the molecules in dielectrics. W. Kliefoth observed the **electrostriction** or contraction in vol. which occurs when an cxternal electric force is applied to the gas; this indicates that the attraction between the molecules is of electrical origin.

M. Faraday said that nitrogen "appears to be neither magnetic nor diamagnetic." F. Zantedischi discussed this subject. The **magnetic susceptibility** found by G. Quincke at 16° was $+0·001\times10^{-6}$ vol. unit at one atm. press., and $+0·04\times10^{-6}$ at 40 atm. press. T. Soné gave $-0·00033\times10^{-6}$ vol. unit at 20°, and $-0·265\times10^{-6}$ mass unit for chemically pure nitrogen; and $-0·000360\times10^{-6}$ vol. unit and $-0·452\times10^{-6}$ mass unit for atm. nitrogen. F. J. von Wisniewsky gave $-4·91\times19^{-10}$ mass units. L. G. Hector gave $-49·1\times10^{-7}$ for the vol. susceptibility of nitrogen at 20° and 760 mm.; P. Pascal calculated for combined nitrogen $-55·5\times10^{-7}$. The subject was studied by G. W. Hammar. According to A. Glaser, as the press. of the nitrogen is diminished, the susceptibility at first decreased in proportion; but this ceased when a definite press. was attained, and thereafter, the rate of the diminution of the susceptibility decreased greatly, so that at very low press. the susceptibility is three times as great as it could have been if the original rate of diminution had been maintained throughout. He suggested that at low press., the distancc between the mols. is such that there is time between the collisions for the mols. to become oriented with respect to the field. At higher press., the collisions are constantly destroying any tendency to orientation, so that all the mols. are practically unoriented. G. Breit found the susceptibility to be proportional to the press. if that be sufficiently high or sufficiently low, but there is an intermediate region where the relation is non-linear. B. H. Wilsdon calculated values for the magnetic constants. N. C. Little observed a fall in temp. when nitrogen is excited between the poles of an electromagnet.

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§ 7. The Solubility of Nitrogen

J. Priestley[1] observed that nitrogen is given off when water freezes, and hence inferred that water is converted into nitrogen during the operation, or else it contains more nitrogen in soln. than is usually suspected, but H. Davy showed that the gas is only in soln. as common air. Nitrogen is soluble in water. N. T. de Saussure said that one vol. of water at 18° dissolves 0·0417 vol. of nitrogen, 0·0147 vol. at 15·5° according to W. Henry; and, according to J. Dalton, 0·0156 vol. at ordinary temp. Observations were also made by R. Bunsen, W. E. Adeney and H. G. Becker, K. Angström, J. H. Coste, C. Jäger, B. Schulz, T. E. Thorpe and J. W. Rodger, E. B. Truman, M. Trautz and H. Henning, F. Weigert, C. J. J. Fox, K. Drucker and E. Moles, C. Müller, A. Findlay and H. J. M. Creighton, G. Just, L. Braun, G. von Hüfner, W. Dittmar, A. Hamberg, J. H. Hildebrand, O. Petterson and K. Sodén, and C. Bohr and J. Bock. A selection from the results of L. W. Winkler is given in Table XI, where the **absorption coefficient,** β, represents the vol. of gas, reduced to 0° and 760 mm., which is absorbed by one vol. of liquid when the press. of the gas, without the partial press. of the liquid, amounts to 760 mm.; the **solubility,** S, represents the vol. of gas reduced to 0° and 760 mm., absorbed by one vol. of the liquid when the barometer indicates 760 mm.; and, q, the weight of gas in grams taken up by 100 grms. of liquid at the indicated temp., and when the partial press. of the gas plus the vap. press. of the liquid totals 760 mm. H. E. Roscoe and J. Lunt said that a litre of water sat. with air contains

TABLE XI.—THE SOLUBILITY OF NITROGEN IN WATER.

Temp.	β	S	q	Temp.	β	S	q
0°	0·02348	0·02334	0·00239	50°	0·0109	0·00955	0·00121
1°	0·02291	0·02276	0·00	55°	—	—	—
5°	0·02081	0·02063	0·00259	60°	0·0102	0·00822	0·00105
10°	0·01857	0·01834	0·00259	65°	0·00996	0·00751	0·00094
15°	0·01682	0·01654	0·00230	70°	0·00976	0·00676	0·00085
20°	0·01542	0·01507	0·00208	75°	0·00963	0·00597	0·00075
25°	0·01432	0·01387	0·00189	80°	0·00957	0·00510	0·00069
30°	0·01340	0·01284	0·00174	85°	0·00954	0·00410	0·00052
35°	0·01254	0·01185	0·00161	90°	0·00952	0·00294	0·00037
40°	0·01183	0·01097	0·00148	95°	0·00949	0·00158	0·00020
45°	0·01129	0·01023	0·00128	100°	0·00947	0·0000	0·00000

15·47 c.c. of nitrogen, and 7·87 c.c. of oxygen at 0°; at 15°, 13·83 c.c., and 7·09 c.c. of oxygen; at 20°, 12·76 c.c., and 6·44 c.c. of oxygen; and at 25°, 11·78 c.c., and 5·91 c.c. of oxygen. Observations were also made by E. Ruppin, G. C. and M. C. Whipple, A. Hamberg, W. Dittmar, and O. Pettersson and K. Sodén—*vide* air. R. Bunsen represented the coeff. of absorption, at $\theta°$, by $\beta=0{\cdot}020346-0{\cdot}00053887\theta+0{\cdot}000011156\theta^2$. The solubility of nitrogen in *sea-water* was measured by C. J. J. Fox, W. Dittmar, J. H. Coste, A. Hamberg, and H. Tornoë. L. Cassuto measured the effect of pressure, *p* in metres of mercury, on the solubility coeff. of nitrogen in water, and found:

19·4°	*p*	0·8910	1·2488	2·9074	4·5958	6·2767	7·5815	8·1074
	S	0·01617	0·01611	0·01585	0·01554	0·01515	0·01487	0·01473
24·9°	*p*	0·8977	1·15573	2·5171	4·0947	5·0529	7·0333	8·1846
	S	0·01498	0·01487	0·01478	0·01440	0·01429	0·01382	0·01369

K. S. Wyatt found that an aq. soln. of nitrogen, saturated at a press. exceeding 100 atm. at ordinary temp., could be brought to atm. press. without the immediate formation of bubbles in the body of the liquid; and F. B. Kenrick and co-workers studied the supersaturation of water with nitrogen. W. E. Adeney and H. G. Becker measured the *rate of solution* of nitrogen in water and found that $dw/dt=a-bw$, where w represents the total quantity of gas in soln. at any moment; t, the time; and a and b are constants depending on the size of the apparatus. The rate of solution depends on the humidity of the gas, being greater with dry than with moist air. J. Metschel discussed the supersaturation of nitrogen in water. I. R. McHafie studied the conc. of water in the gas phase with air in equilibrium with water. F. Garelli and E. Monath observed no appreciable lowering of the f.p. of stannous chloride by the dissolution of nitrogen.

E. Erdmann and F. Bedford found that liquid *oxygen* absorbs nitrogen energetically from the atm. At −191·5°, 14·880 grms. of liquid oxygen absorb 5–6 litres of gaseous nitrogen at the same time almost doubling its vol. A. Stock made some observations on this subject—*vide* the vap. press. of liquid air. For the coeff. of absorption of nitrogen by *sulphuric acid*, C. Bohr found between 20·9° and 21·5°:

H_2SO_4	0	4·9	10·7	20·3	29·6	34·3	35·8
β	0·0156	0·0091	0·0066	0·0049	0·0051	0·0100	0·0129

Measurements were also made by A. Christoff. L. Braun gave for the coeff. of absorption of nitrogen in aq. soln. of *sodium chloride* and of *barium chloride*:

	0°	5°	10°	15°	20°	25°
NaCl	0·6 per cent.	0·0200	0·0185	0·0164	0·0148	0·0130
	11·73 ,, ,,	0·0102	0·0093	0·0081	0·0066	0·0047
$BaCl_2$	3·33 ,, ,,	0·0183	0·0168	0·0150	0·0135	0·0119
	13·83 ,, ,,	0·0127	0·0117	0·0104	0·0092	0·0078

J. H. Coste and E. R. Andrews measured the solubility of nitrogen in soln. of sodium, *potassium and ammonium chlorides;* and A. T. Larsen and C. A. Black, in liquid *ammonia*. N. T. de Saussure said that 100 vols. of either water or alcohol of sp. gr. 0·84 dissolve 4·2 vols. of nitrogen at 18° and 760 mm. The solubility of nitrogen is greater in *alcohol* than in water. R. Bunsen gave for the absorption coeff.:

	0°	5°	10°	15°	20°	24°
β	0·1263	0·1244	0·1228	0·1214	0·1204	0·1198

L. Carius gave $\beta=0{\cdot}126338-0{\cdot}000418\theta+0{\cdot}0000060\theta^2$. Observations were also made by G. Just, and S. Gniewasz and A. Walfisz. J. Metschel discussed the supersaturation of soln. in alcohol. For the solubility expressed as the ratio of the vol. of gas absorbed at any given temp. and press. to the vol. of the absorbing liquid, or the vol. of gas absorbed per unit vol. of solvent, G. Just found at 20° and 25°

respectively for water, 0·01705 and 0·01634; *methyl alcohol*, 0·1348 and 0·1415; *ethyl alcohol* (99 per cent.), 0·1400 and 0·1432; *amyl alcohol*, 0·1208 and 0·1225; *isobutyl alcohol*, 0·1701 and 0·1734. J. W. Döbereiner said that ether absorbs 0·15 vol. of nitrogen, and A. Christoff found the solubility of nitrogen in *ether* at 0° is 0·2580, and at 10°, 0·2561. G. Just gave for the solubility at 20° and 25°, respectively, *aniline*, 0·02992 and 0·03074; *sulphur dioxide*, 0·05290 and 0·05860; *nitrobenzene*, 0·06082 and 0·06255; *benzene*, 0·1114 and 0·1159; *acetic acid*, 0·1172 and 0·1190; *xylene*, 0·1185 and 0·1217; *toluene*, 0·1186 and 0·1238; *chloroform*, 0·1282 and 0·1348; *acetone*, 0·1383 and 0·1460; *amyl acetate*, 0·1512 and 0·1542; and *ethyl acetate*, 0·1678 and 0·1727. J. H. Hildebrand expressing the solubility in terms of the molar fraction $N\times10^4$ when the press. p is 1 atm., at 20°, found for the solubility of nitrogen in xylene, 6·1; ethyl acetate, 6·8; toluene, 5·3; chloroform, 4·3; benzene, 4·1; acetone, 4·2; ethyl alcohol, 3·3; nitrobenzene, 2·6; methyl alcohol, 2·2; aniline, 1·1; *carbon disulphide*, 1·3; and water, 0·13. G. Tammann also measured the solubility of nitrogen in ethyl, methyl, and amyl alcohols, benzene, aniline, carbon disulphide, *isobutyl, and amyl acetates*, ethylacetate, benzene, toluene, xylene, nitrobenzene, acetone, acetic acid, and chloroform. S. Gniewasz and A. Walfisz gave for the absorption coeff. of nitrogen in *petroleum* at 10°, 0·135; and at 20°, 0·117. L. Braun gave for 3·82 per cent. aq. soln. of *propionic acid*, 0·0209 at 5° and 0·0137 at 25°; and for 11·22 per cent. soln., 0·0195 at 5° and 0·0130 at 25°. K. Drucker and E. Moles gave 0·1640 for the solubility of nitrogen in *isobutyric acid* at 25·05° and 388·3 mm., and 0·1656 at 832·2 mm.; for 37·5 per cent. isobutyric acid at 23·02° and 246·2 mm., 0·0393 and at 867·3 mm. press., 0·0401; and at 29·02° and 231 mm., 0·0373, and 720 mm. press., 0·0386. L. Braun gave for 2·28 per cent. aq. soln. of *urea*, 0·0199 at 5°, and 0·0139 at 25°; and for 15·65 per cent. soln., 0·0175 at 5°, and 0·0130 at 25°. C. Bohr said that *blood* absorbs relatively more nitrogen than water. A. Findlay and H. J. M. Creighton found that the solubility of nitrogen in blood, or in *serum*, is less than in water. C. Himly said that one vol. of *caoutchouc* absorbs 5 vols. of nitrogen in 5 weeks. G. Just said that the solubility of nitrogen in *glycerol* is immeasurably small at 20°–25°. C. Müller, and A. von Hammel measured the solubility of nitrogen in glycerol and *chloral hydrate*. The latter gave at 15°:

Chloral hydrate	0	6·9	14·0	26·1	49·3	70·9	79·1 per cent.
β	0·01706	0·0164	0·0154	0·0141	0·0118	0·0131	0·0156
Glycerol	0	15·7	29·9	46·6	72·8	87·3	99·25 per cent
β	0·1707	0·01400	0·01087	0·00840	0·00552	0·00493	0·00524

C. Müller found for 11·38, 29·93, and 48·57 per cent. soln. of *sucrose*, at 15°, β=0·01480, 0·01053, and 0·00700 respectively; and G. von Hüfner gave at 20·16°–20·25°, the coeff. of absorption, β=0·01215, 0·01380, and 0·01480 for N, 0·5N-, and 0·25N-soln. of *dextrose;* 0·01221, for N-soln. of *lævulose;* 0·1203, *arabinose;* 0·01321, *erythritol;* 0·01213, *alanine;* 0·01212, glycerol; 0·01477, *urea;* and 0·01475, *acetamide.* J. Metschel discussed the supersaturation of soln. in ethyl alcohol, benzene, nitrobenzene, and aniline.

M. Berthelot[2] found quartz permeable to nitrogen at 1300°—*vide quartz* and glass. The adsorption of nitrogen by *platinum* has been studied by T. Graham, W. Hempel and G. Vater, and A. Sieverts; *iron, chromium, manganese, aluminium,* and *magnesium*, by A. P. Lidoff; *copper, silver*, iron, and *nickel*, by A. Sieverts and co-workers; silver, by F. Durau; *sodium*, copper, iron and nickel, by W. A. Dew and H. S. Taylor; *carbon*, by W. Hempel and G. Vater, F. Bergter, H. Briggs, G. Claude (at −182·5), G. Craig, J. Dewar, I. F. Homfray, J. Hunter, A. B. Lamb and co-workers, H. H. Lowry and S. O. Morgan, E. Reichardt, and A. Titoff. A. B. Berthollet observed that nitrogen adheres very tenaciously to *charcoal*—for the absorption by charcoal, *vide* carbon. J. B. Firth, R. E. Wilson, W. E. Garner, R. Chaplin, F. G. Keyes and M. J. Marshall, and S. McLean studied the adsorption of the gas by charcoal. A. G. R. Whitehouse gave 0·17–0·22 cal. per c.c., and

F. G. Keyes and M. J. Marshall, 3654 cals. per mol. for the heat of adsorption of nitrogen by charcoal. H. Rowe studied the adsorption at low press. The adsorption of nitrogen by *caoutchouc* was studied by T. Graham, A. d'Arsonval, H. A. Daynes, G. von Hüfner, and C. S. Venable and T. Fuwa ; *kieselguhr, pumice-stone, bone-ash,* and *iron-ore,* by W. Hempel and G. Vater ; *silica, stannic acid, alumina,* and *meerschaum,* by H. Briggs ; *mica,* by B. Iliin, and I. Langmuir ; *soils,* by H. E. Patten and F. E. Gallagher, and E. Reichardt ; *glass,* by I. Langmuir, F. Durau, F. H. Newman, and N. R. Campbell and co-workers ; *zinc oxide,* by H. N. Morse and H. B. Arbuckle, and T. W. Richards and E. F. Rogers ; *chabazite,* by R. Nacken and L. Wolff, and R. Seeliger ; *silica-gel,* by L. H. Reyerson and L. E. Swearingen ; and *iron hydroxides,* by F. Scheermesser. J. D. Edwards and S. F. Pickering found that if the permeability of rubber to hydrogen is unity, the value for nitrogen is 0·16.

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§ 8. The Chemical Properties of Nitrogen

What of nitrogen? Is not its apparent great simplicity of action all a sham?—M. FARADAY.

Was kamm Wohl die Ursache sein, dass der Stickstoff, in seinen Vereinigungen seine Natur verandert?—J. J. BERZELIUS.

Nitrogen is the essentially romantic element, devil or god, according to circumstances.—*Lancet.*

Nitrogen at first sight appears to have but a small tendency to take part in chemical reactions. The negative behaviour of nitrogen is illustrated by the fact that it does not burn in air like hydrogen, and does not support combustion like oxygen. Its presence in a gas is assumed because of its inactivity; it does not respond to any of the usual tests. In fine, the most obtrusive characteristic of nitrogen is its chemical inertness, due, it is sometimes stated to " the great affinity of the atoms in the molecule for one another "; but, as G. Martin[1] has said, nitrogen possesses very powerful affinities for certain elements and very feeble affinities for others, just in the same way as oxygen or sulphur possesses very strong affinities for some elements and feeble ones for others, the only difference being that nitrogen exerts its greatest attraction on elements which are different from those upon which oxygen or chlorine exerts its greatest affinity. Nitrogen combined with other elements often exhibits great chemical activity. Nitrogen is the dominant element in the proteins—the essential constituent in our foods. It has been said that without proteins we die, this means that without nitrogen we die. It is a conspicuous element in hæmoglobin, and in the enzymes. There are other conspicuous nitrogen compounds like prussic acid, the alkaloids, artificial musk, indigo, and the azo-dyes. Nitrogen is the central figure in the chemistry of war, for it is an essential constituent of virtually all the useful explosives. In illustration, nitrogen chloride is possibly the most violent explosive known—but its energy is not sufficiently under control to allow it to be harnessed for use; potassium nitrate is the active agent in gunpowder; and the white and smokeless powders, and explosives are all nitrogenous—*e.g.* nitroglycerol, picric acid, trinitrotoluene, gun-cotton, etc. The power of nitrogen in explosives depends on the fact that when associated with oxygen it easily releases its partner, which is then taken up by the associated elements or compounds. The resulting oxidation occurs with explosive rapidity, and huge volumes of gas are formed instantaneously. At the same time, the nitrogen returns to what appears to be a more congenial state—gaseous nitrogen. In breathing, about 450 galls. of nitrogen pass through the lungs every 24 hrs., and this quantity would be sufficient to make 30 lbs. of nitrotoluene, or 40 lbs. of gun-cotton.

The idea that nitrogen is an inert gas with a disinclination to enter into chemical reactions is now said to be an ancient fiction; but it is still true that nitrogen is inert in the sense that it is difficult to initiate reactions in which free nitrogen takes part. It is usually necessary to raise the reacting components to a high temp. in order to inaugurate the reaction. This shows that nitrogen leaves its "state of chemical rest" with difficulty. The chemical inertness of nitrogen is sometimes attributed to the relative stability of the molecules. Once the molecule is under conditions where it must dissociate into atoms: $N_2 \rightleftharpoons 2N$, it becomes very reactive. Hence it requires a high temp. to make nitrogen unite with hydrogen, while iodine unites with hydrogen at a comparatively low temp. because its molecules are comparatively easily dissociated into atoms. In the absence of other data, G. Martin expressed the "affinity" of the elements for one another in terms of their relative heats of dissociation, and plotted, in three dimensions, the affinities of the elements with their group and series numbers in the periodic table, **1.** 6, 3. The relations of an element to the other elements can thus be represented by the distances from a horizontal plane, or by a kind of surface—the so-called *affinity surface.* That for nitrogen is represented by Fig. 7.

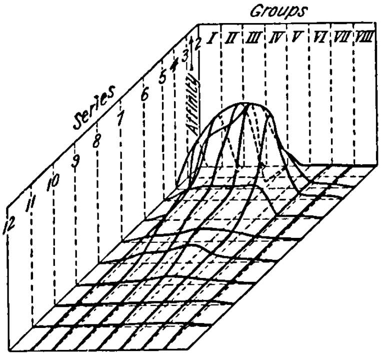

FIG. 7.—G. Martin's Affinity Surface for Nitrogen.

Nitrogen can under certain conditions be made to unite directly with **hydrogen** to form ammonia—*vide infra*—and quite a series of nitrogen hydrides is known. Active hydrogen was found by G. L. Wendt and R. S. Landauer,[2] Y. Venkataramaiah, and H. S. Hirst to act on nitrogen, forming ammonia—*vide infra,* the synthesis of ammonia—but H. S. Taylor, A. L. Marshall and H. S. Taylor, and E. Böhm and K. F. Bonhöffer failed to detect any action on nitrogen. E. J. B. Willey and E. K. Rideal said that nitrogen at 10 mm. press. forms ammonia when in contact with activated hydrogen. According to W. A. Noyes, gaseous hydrogen and nitrogen form ammonia in the presence of mercury vapour—possibly also some hydrazine is formed. The dissociation of the hydrogen caused by the resonance radiation of mercury is taken to be the important factor; and the number of molecules of ammonia formed is of the same order as the number of quanta in the incident radiation. J. N. Pring and E. O. Ransome found that when hydrogen is liberated electrolytically in contact with nitrogen at atm. press., 0·04 per cent. of ammonia was formed; at 60–104 atm., 0·09 per cent.; and at 300–500 atm., none was obtained. Hence the minute yield was due to thermal action, and not to the reaction between nitrogen and cathodic hydrogen—*vide infra,* the synthesis of ammonia. D. Berthelot and H. Gaudechon said that nitrogen and **oxygen** do not combine under the influence of light from a quartz mercury lamp—*vide supra,* the fixation of nitrogen. The direct union of nitrogen with oxygen to form the nitrogen oxides is discussed in connection with the so-called fixation of atm. nitrogen. N. Smith observed no signs of the formation of nitrite or nitrate when moist ferric oxide, stannic oxide, platinum, manganese dioxide, or lead dioxide is exposed to oxygen and nitrogen, nor was there any sign of oxidation of the nitrogen in the presence of tin, or of ferrous or manganous oxide; but some oxidation generally occurred in the presence of zinc, iron, magnesium, potassium, sodium, or cuprous oxide or chloride. W. T. David found that the combustion of hydrogen, carbon monoxide, or methane in air is favoured by ultra-red radiations; while W. T. David and co-workers showed that if the nitrogen of air be replaced by argon, oxygen, carbon dioxide, or the combustible gas itself, the ultra-red radiation has no effect. It is inferred that there is a temporary association between the molecules of nitrogen or of nitrogen oxides with those of the combustible gas tending to retard combustion, but this association is inhibited when the molecules of the combustible gas require vibrational energy by the absorption of ultra-red radiation with a resultant increase in the speed of combustion. Nitrogen is not oxidized by **ozone.** Further observations on the action of oxygen and ozone on nitrogen are discussed in connection with the fixation of nitrogen by oxidation. C. F. Schönbein, and T. S. Hunt supposed that ozone can oxidize nitrogen in the presence of alkalies, but L. Carius, and M. Berthelot were unable to confirm these observations. Both C. F. Schönbein, and M. Berthelot, however, showed that nitrous acid is formed along with ozone during the slow oxidation of phosphorus. Liquid nitrogen is a good solvent for liquids with a low b.p. Thus, H. Erdmann found that it readily dissolves liquid oxygen, and forms a clear blue soln. with liquid ozone. J. K. H. Inglis and J. E. Coates observed a small contraction when liquid oxygen and nitrogen are mixed, and A. Stock and C. Nielsen showed that with eq. proportions at —197°, the temp. rises about 0·5°, and the vol. contracts about 0·5 per cent. According to A. and P. Thénard, a mixture of **water** vapour and nitrogen, under the influence of an electric discharge, furnishes ammonium nitrite; M. Berthelot obtained a similar result with a strong induction current, but not with a feeble one. O. F. Tower observed that only traces of nitric oxide are formed when a mixture of nitrogen and water vap. is passed over an incandescent filament of rare earths at about 2000°. The attempt made by P. Villard to prepare *nitrogen hydrate* was not successful.

The affinity of nitrogen for the **halogens** is small; it is greatest for iodine and least for fluorine. H. Moissan[3] observed no sign of reaction between **fluorine** and nitrogen. O. Ruff and E. Giesel failed to make nitrogen fluoride. With **chlorine,** however, nitrogen forms a chloride (*q.v.*), and P. Hautefeuille and J. Chappius observed that if a mixture of chlorine, oxygen, and nitrogen is sparked, a white solid approximating $N_2Cl_2O_{13}$, or $Cl_2O_7.2NO_3$, is formed. Nitrogen possibly unites indirectly with **bromine** forming a questionable bromide (*q.v.*), and with **iodine** an **iodide** (*q.v.*). The affinity of nitrogen for the elements of the **sulphur** family is small. M. Berthelot[4] noted that nitrogen is oxidized when sulphur is burnt in compressed air in a calorimeter bomb. F. Richarz reported that when a sulphuric acid soln. of **persulphuric acid** is exposed to air, nitrous acid is formed, but M. Traube denied this, and stated that hydrogen dioxide, not nitrous acid, was responsible for the reactions on which F. Richarz based his conclusion. A. T. Larson and C. A. Black measured the solubility of nitrogen in liquid **ammonia** expressed in c.c. of gas at n.p.t. per gram of solvent:

	50 atm.			100 atm.			150 atm.		
	−25·2°	0°	19·0°	−25·0°	0°	22°	−22·0°	5·0°	13·3°
S	0·72	1·15	1·46	1·35	2·28	3·21	1·89	3·33	3·61

The affinity of nitrogen for the elements of the **phosphorus** family is feeble; nitrogen forms a phosphide. H. Moissan[5] found **tantalum** forms a nitride when heated to a high temp. in an atm. of nitrogen. The affinity of nitrogen for the elements of the **carbon** family is small. B. Iliin studied the adsorption of nitrogen by the carbon. O. Warburg and W. Brefeld discussed the activation of the iron in catalytic charcoal by nitrogen. M. Berthelot found that dried carbon does not unite with dry nitrogen under the influence of the electric discharge, but if water or hydrogen be present, **acetylene** is formed, and this with the nitrogen furnishes hydrogen cyanide. The reaction between acetylene and nitrogen was studied by W. E. Garner and co-workers. C. Lüdeking found that cyanogen is formed in the combustion of carbon in air. The synthesis of cyanides by the action of nitrogen on heated carbon, or on the carbon arc, was studied by J. E. Bucher, C. T. Thorssell, P. Askenasy and F. Grude, A. Frank and N. Caro, W. Moldenhauer and O. Dieffenbach, J. Moscicky, and A. König and W. Hubbuch. M. Berthelot found nitrogen is oxidized when carbon is burnt in compressed air in a calorimeter bomb; and he observed that under the influence of the silent discharge, nitrogen is absorbed by a number of organic products—**methane, benzene, terebenthine, cellulose, dextrin, thiophene, carbon disulphide,** etc. The influence of nitrogen on the speed of propagation of flame was examined by R. V. Wheeler and co-workers, H. B. Dixon, O. C. de C. Ellis and co-workers. H. Crouch and E. K. Carver studied the effect of nitrogen on the explosion limits of mixtures of methyl alcohol and of acetone with air. F. Garelle noted the tendency of nitrogen dissolved in benzene, bromoform, nitrobenzene, and cyclohexane to enter the solid phase and lower the f.p. about 0·005°. S. Miyamoto found that complex products were formed when mixtures of nitrogen with benzene or with ethylene are used. M. Berthelot, L. Hock, S. M. Losanitsch and M. Z. Jovitschitsch, S. M. Losanitsch, E. Briner and A. Baerfuss, E. Briner and E. L. Durand, H. P. Kaufmann, W. Loeb, L. Francesconi and A. Ciurlo, W. Dominik, A. König and W. Hubbuch, and E. Schüpbach studied the action of the silent discharge on mixtures of nitrogen and methane.

F. Wöhler and H. St. C. Deville showed that only at a white-heat does **silicon** react with nitrogen to form a nitride; H. Moissan observed a similar result with **titanium,** at about 800°; and J. W. Mallet, and E. Wedekind with **zirconium** at about 1000°. H. Moissan found that boron forms a nitride at a temp. above 1000°, but the affinity of nitrogen for aluminium and the other elements of that family is feeble. A. Rossel made a nitride of **aluminium,** and H. Moissan, and C. Matignon made nitrides of **thorium, cerium, lanthanum, praseodymium, neodymium,** and **samarium** by heating these elements in an atm. of nitrogen at a high temp. G. Ferée made **chromium** nitride in a similar way; H. Moissan, **tungsten** nitride, and **uranium** nitride, and A. Rossel, **iron** nitride. In the **magnesium** family, the affinity of nitrogen probably reaches a maximum with magnesium, and then falls to a low value towards zinc and thallium. H. St. C. Deville and H. Caron,[6] F. Brieglez and A. Geuther, and A. Rossel made magnesium nitride by heating the metal in an atm. of nitrogen. H. Erdmann found a burning magnesium wire is extinguished when plunged in liquid nitrogen. L. Maquenne, H. Moissan, A. Güntz, and A. Geuther made the nitrides of the alkaline earths—**barium, strontium,** and **calcium.** H. Erdmann said that a mixture of liquid nitrogen and calcium cannot be ignited in the ordinary way, but it can be ignited by a thermite cartridge. L. Ouvrard, and H. Deslandres made the nitride of **lithium** by direct union of the elements. The affinity of nitrogen for the alkaline earths and copper, silver, and gold steadily decreases from lithium to gold. R. Blondlot made **copper** nitride. G. Tammann observed that copper, and iron form much nitride when heated in nitrogen; cerium, lanthanum, **manganese,** chromium, **vanadium,** and titanium change colour; while silicon, **tantalum,** tungsten, **molybdenum, cobalt,** and **nickel** do not change colour.

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§ 9. Allotropic Forms of Nitrogen

Near the beginning of the nineteenth century, there was some discussion as to whether nitrogen is an element or a compound. The controversy as to the possibility of nitrogen being a compound substance with water as the ponderable base recalls a similar dispute as to whether or not carbonic acid exists in chalk. Nitrogen was produced by passing water through a red-hot tube. G. Pearson,[1] and W. Henry obtained nitrogen by burning hydrogen and oxygen in hermetically sealed vessels; J. Priestley, by allowing oxygen to stand in contact with water; C. Girtanner, by boiling water in a glass vessel; and F. H. A. von Humboldt, by allowing earths to stand in a vessel containing atm. air whereby air is changed into nitrogen. Hence, said G. Girtanner, nitrogen is water deprived of its oxygen; or J. Mayer, nitrogen is composed of oxygen and hydrogen. J. C. Wiegleb, J. F. A. Göttling, F. Wurzer, and L. von Crell held similar views. It was shown by A. W. van Hauch, C. W. Jach, J. B. van Mons, N. T. de Saussure, C. L. Berthollet, and J. R. Dieman and co-workers, that "the nitrogen gas which, in some cases, is obtained by passing water-vapour through ignited tubes, proceeds merely from the external air, deprived of its oxygen by the fire in which the tubes are placed; and the supposed conversion of water into nitrogen, by combination with the matter of heat, is overthrown." Those who had synthesized nitrogen in other ways were also deceived by experiments in which the solubility of nitrogen in water, and the contamination of their gases, etc., with air was overlooked. This was not obvious because J. J. Berzelius, for instance, considered nitrogen to be a suboxide of an unknown element which he called *nitricum*. Ordinary nitrogen was supposed to be a compound of about 43 parts of nitricum and 57 parts of oxygen. The at. wt. of nitricum was given as 12·1–12·7. In 1809, H. Davy also stated: The decomposition and composition of nitrogen seem proved, and one of its elements appears to be oxygen; but what is the other elementary matter? Or is it that nitrogen is a compound of hydrogen with a larger proportion of oxygen than exists in water? In 1812, H. Davy agreed that nitrogen is an element. In 1820, J. J. Berzelius had given up nitricum, and, consonant with the ideas of A. L. Lavoisier, J. Dalton, and J. L. Gay Lussac, he recognized that the elementary nature of nitrogen is the only hypothesis in accord with the definition of an element. In 1862, T. S. Hunt called nitrogen, *le nitrile de l'acide azoteux*.

A. Morren,[2] E. Sarasin, E. Warburg, E. Goldstein, and E. P. Lewis noted that on passing a condensed induction discharge through rarefied nitrogen, a brilliant yellow luminescence is obtained, and that this luminescence persists for a considerable time after discontinuing the discharge. R. J. Strutt investigated the phenomenon, and showed that the gas in this condition can take part in many reactions which do not occur with ordinary nitrogen. An apparatus suitable for the purpose is illustrated diagrammatically in Fig. 8. A current of attenuated nitrogen is supposed to be passing along the tube *A* through which a jar discharge is passing. As the nitrogen passes into the vessel *B*, it appears as a "whirling cloud of brilliant yellow light." The luminous gas was found by A. Fowler and R. J. Strutt to give a characteristic spectrum showing green, yellow, and red bands of about equal intensity. According to R. J. Strutt, if the tube through which the gas is passing be heated at one point, the glow disappears, and if the tube be strongly heated, the glow is permanently extinguished. The intensity of the glow is increased by cooling in liquid air, but the glow is extinguished in the coldest part of the vessel. E. Tiede and E. Domcke stated that the after-glow of the active nitrogen that had been passed over heated copper is suppressed unless oxygen has been added to the nitrogen. The phosphorescence of sulphur, iodine, sodium, and other bodies which occurs when they are heated in nitrogen, through which has been passed an electric discharge, is attributed to the presence of oxygen, and not to the nitrogen having been rendered active. On the other hand, A. König and E. Elöd have shown that the phosphorescence will take place in nitrogen, free from every trace of oxygen, provided that metallic vapours, such as those of mercury, are also excluded. The glow is suppressed by the presence of a mere trace of mercury vapour, such as would be derived from the pump and manometer. On admitting a little oxygen, this mercury is oxidized, and the glow reappears, while the introduction of still more oxygen extinguishes it. H. B. Baker and R. J. Strutt also showed that the activation of nitrogen is not produced by traces of oxygen because nitrogen from which every trace of oxygen has been eliminated still showed the phenomenon, as did also the nitrogen prepared from potassium azide. Moreover, contrary to E. Tiede and E. Domcke, commercial nitrogen from a cylinder remained "active" after having been passed over copper heated to 400° to remove any residual oxygen. As a further proof that "active" nitrogen is a distinct modification of the element, there is the fact that it enters into combination with other substances. For example,

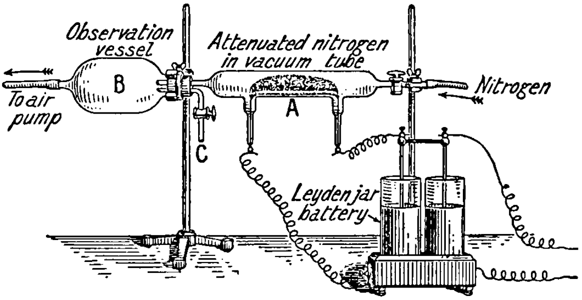

FIG. 8.—The Preparation of Active Nitrogen.

it acts upon different metals, such as mercury, to form nitrides ; while it decomposes certain organic compounds, with the formation of hydrogen cyanide. J. Kowalsky also confirmed these observations ; he observed the same phenomena with nitrogen from which special precautions were taken to eliminate every trace of oxygen. The orange glow of the " active nitrogen " was preceded by a series of minute explosions and an intense violet fluorescence. The explosions were attributed to the interaction of the active nitrogen and the mercury vapour, resulting in the formation of an explosive mercury nitride. The presence of mercury vapour (derived from the pump) in the gas was proved spectroscopically—the violet light showed the spectrum of mercury. Similar results were obtained by R. J. Strutt, M. Pirani and E. Lax, and F. Comte. A. G. Worthing and R. Rudy observed the excitation of the line spectrum of tungsten and nickel by activated nitrogen; and R. S. Mulliken, the excitation of the spectra of the copper halides. S. Karrer and co-workers examined the electrical conductivity of active nitrogen ; and N. H. Ricker, the luminosity. P. K. Kichlu said that the active nitrogen carries no free charge, and no charged particle of N_2. When sodium is acted on by activated nitrogen, the metal is ionized. A. G. Worthing studied the discharge of activated nitrogen; and C. Kenty and L. A. Turner, the surface layers of activated nitrogen on tungsten.

The nitrogen which has been exposed to the electric jar-discharge, is very active chemically, and is sometimes termed **activated nitrogen.** If the nitrogen be pure it does not become active under the influence of the jar-discharge—*vide supra*. The presence of a trace of foreign matter—oxygen, methane, ethylene, carbon oxides, hydrogen sulphide, or mercury vapour—is necessary for its production ; and N. R. Dahr also noted that the after-glow of nitrogen is increased by the presence of some of these gases. According to R. J. Strutt, the amount of oxygen necessary to produce the greatest effect gradually increases until it reaches a maximum of one part in 500, after which, the intensity of the glow decreases; and with 2 per cent. oxygen, the activity is destroyed. For the action of activated nitrogen on *oxygen*, and *ozone*, see the fixation of nitrogen by oxidation. Activated nitrogen gradually returns to normal nitrogen on standing, and very rapidly in the presence of oxidized copper. According to T. M. Lowry, air that has been subjected first to a silent and then to a sparking electric discharge shows the spectrum of nitrogen peroxide, apparently formed by the oxidation of a variety of nitrogen produced under the influence of the discharge. After a few seconds, this oxidizable kind of nitrogen reverts to a form which can no longer be oxidized either by oxygen or by ozone. R. J. Strutt's chemically active nitrogen is not oxidized by ozone under the conditions indicated above. The spectrum, etc., of the nitrogen after-glow was discussed by R. Rudy, E. P. Lewis, R. J. Strutt, R. T. Birge, A. E. Ruark and co-workers, K. T. Compton, A. S. Levesley, R. C. Johnson and H. G. Jenkins, and W. H. B. Cameron. It consists of the so-called α-, β-, and γ-groups—partly in the visible region and partly in the ultra-violet. The group supposed to originate from a metastable N_2 mol., lies in the red, yellow, and green ; the other groups, originating from a metastable NO molecule, are chiefly in the ultra-violet. R. C. Johnson and H. G. Jenkins did not find any other group in the ultra-violet. P. D. Foote and co-workers studied the energy of activated nitrogen; and E. J. B. Willey said that the heat of formation, -43 Cals. per mol., does not agree with the assumption that active nitrogen is atomic.

E. P. Lewis found that active nitrogen excites a strong green or bluish-green phosphorescence with uranium nitrate, uranium ammonium fluoride, zinc sulphide, barium chloride, strontium chloride, calcium chloride, and cæsium chloride, whereas a weak effect is given by lithium chloride, sodium chloride, potassium chloride, sodium iodide, potassium iodide, sodium carbonate, and strontium bromide. The phenomenon may be due to chemical reaction with the active nitrogen, or to the presence of free electrons. W. Jevons observed that the vap. of aluminium chloride produced a solid deposit which exhibited a bright green phosphorescence, but

H. Krepelka obtained no phosphorescence with aluminium bromide. E. Tiede and A. Schleede found that the phosphorescence is also shown by lithium fluoride, lithium carbonate, beryllium carbonate, beryllium oxide, barium platinicyanide, magnesium carbonate, calcium hexanitride, barium hexanitride, molybdic acid, terephthalic acid, and *iso*phthalic acid. It is noted that all these compounds contain nitrogen or an element of small atomic number. Sulphides and oxides of the second group of the periodic system show little or no effect. Ozone can also induce phosphorescence. The phenomenon is supposed by K. N. Bönhoffer and G. Kaminsky to be due to chemiluminescence, in which the decomposition of the activating substance furnishes the energy for luminescence. W. A. Bone and co-workers discussed the activation of nitrogen during the explosion of mixtures of air and carbon monoxide.

R. J. Strutt observed no chemical action between activated nitrogen and *oxygen*, or *hydrogen*. Activated nitrogen gives a bright blue flame with *iodine* vapour; and a pale blue flame with *sulphur*. When in contact with *sulphur chloride*, yellow nitrogen sulphide is formed; and with *carbon disulphide*, a blue polymerized nitrogen sulphide, and a polymerized carbon monosulphide are formed. Activated nitrogen reacts with *hydrocarbons* like *methane*, *pentane*, and *acetylene* to form hydrogen cyanide; when an acetylene flame is fed with a little activated nitrogen, the spectrum in each case shows the cyanogen bands. Solid and liquid products are formed along with the hydrogen cyanide: $C_2H_2+2N=2HCN$. Neither A. König and A. Elöd, nor E. J. B. Willey and E. K. Rideal observed any reaction with methane. R. J. Strutt observed a reaction with other organic vapours—*methyl bromide*, *ethyl iodide*, *chloroform*, *ethylene dichloride*, or *ethylidene dichloride*, *carbon tetrachloride;* and *benzene* appears to yield cyanobenzene—then cyanogen chloride is formed. Activated nitrogen reacts with *nitric oxide*, forming nitrogen peroxide in accord with the curious reaction: $2NO+N=NO_2+N_2$. The change is accompanied by a greenish-yellow flame resembling that produced when ozone reacts with nitric oxide. Activated nitrogen unites with ordinary *phosphorus*, some of which is simultaneously converted into the red form. It is not uncommon to find a mass of phosphorus behaving in a similar way when this element reacts with another substance. Activated nitrogen reacts with *arsenic* developing at the same time a faint green flame. The active nitrogen unites with the vapour of *mercury*, *sodium*, *cadmium*, or *zinc*, forming nitrides, which, when treated with alkali-lye or water, furnish ammonia. The product with mercury is explosive. White deposits containing combined nitrogen are formed when activated nitrogen reacts with *stannic chloride* or *titanic chloride*. In agreement with their hypothesis on the nature of active nitrogen—*vide infra*—E. J. B. Willey and E. K. Rideal found that chemical reaction with active nitrogen and other gases occurs only when the second gas has a critical increment below 55,000 to 60,000 cals. per mol. Thus no reaction occurs with hydrogen (heat of dissociation, 75,000–80,000 cals. per mol); oxygen; carbon monoxide; methene (80,000 cals. for the C—H-linkage); nitrous oxide (60,030 cals. per mol); and hydrogen chloride (90,000 cals. per mol). Reaction occurs with ammonia; nitric oxide (55,000 cals. per mol); hydrogen bromide (50,000 cals. per mol); hydrogen iodide (45,700 cals. per mol); the action with iodine (34,500 cals. per mol) is very marked; less so with bromine (46,200 cals. per mol); and still less so with chlorine (55,000 cals.).

R. J. Strutt suggested as a trial hypothesis that activated nitrogen is nitrogen in the atomic condition, although its chemical relationship to ordinary nitrogen resembles that between ordinary oxygen and ozone. Its production by the discharge: $N_2\rightleftharpoons 2N$ is a reversible reaction which attains a certain limit which is lowered if the conditions be less favourable. Thus, the gas should be at a low press., say a few mm. of mercury, since the collision of atomic with ordinary nitrogen mols. appears to destroy the activity; an uncondensed discharge, without the jar, or a steady high tension continuous current also destroys the activity. In support of this hypothesis there is also the anomalous behaviour of the after-glow in being sustained by heating, and destroyed by cooling—*vide supra;* and E. von Angerer's, and E. J. B. Willey and E. K. Rideal's observations that the reaction is bimolecular, for the rate at which the luminosity of active nitrogen disappears follows the bimolecular rule. The duration of the after-glow is about 30 seconds. At first, the glow is orange-yellow, and slowly changes to greenish-yellow. M. Duffieux favoured a second hypothesis, *viz.*, that the activation of nitrogen is produced by ionized atoms. He said that if the first positive group of nitrogen bands is ascribed to a diatomic mol. of mass 28, the second positive group (which predominates in the discharge on activation of nitrogen) and the negative group are due to the atom of mass 14 rather than to a metastable diatomic mol. In the conditions attending the emission of the two groups of bands, nitrogen atoms are present which are more likely to emit a band spectrum than none at all; the line spectrum attributed to the nitrogen atom is probably due to an ionized atom.

There is the third hypothesis that the activity is produced by unstable molecules. N. R. Dhar supposed that activated nitrogen is produced by the charging of the molecule to a certain potential by the electrical discharge, and that the activity is conditioned by the ease with which the molecules can give up their charge of energy. The luminescence is produced when the charge of energy is given up in the passage from the active to the inactive form. M. N. Saha and N. K. Sur inferred that active nitrogen consists of metastable N_2-mols. loaded with energy equivalent to 8·5 volts, because the spectrum of active nitrogen shows only those positive nitrogen bands attributed to non-ionized N_2-mol., and none of the line spectrum of nitrogen, or even the negative bands supposedly due to $N_2{}^+$. The excitation of the spectra of other materials by active nitrogen is due to the transference of the energy of the metastable state to the atoms of the other substances. In accordance with this view, no lines requiring more than 8·5 volts for their excitation are developed. Hydrogen and the inert gases have no influence on active nitrogen except a mere dilution of the glow. This is in accordance with the fact that the minimum excitation potential of these gases is much higher than the maximum energy which can be transferred by active nitrogen. This view is supported by R. J. Strutt's observation that nitrogen is activated to some extent by excited helium (19·2 volts). E. J. B. Willey and E. K. Rideal added that the argument is weakened by considering the effects of chemiluminescence since the heats of formation of the nitrides of magnesium, calcium, and barium are respectively of the order of 120,000, 112,000, and 199,000 cals. per mol. If the formation of magnesium nitride occurred through interaction between a metastable mol. of nitrogen with an energy of excitation of 2–3 volts and inactive magnesium, then the total energy liberated in combination, if expelled as monochromatic radiation, would be of the order of 8·5 volts. The passage of warm nitrogen over finely-divided magnesium does in fact produce chemiluminescence, a phenomenon more readily observed in the case of lithium. In addition, excited mercury atoms (4·9 volts) readily excite molecular hydrogen, whereas active nitrogen fails to do so. In support of the hypothesis that active nitrogen is nitrogen in a metastable, molecular form, R. J. Strutt found that the energy content of active nitrogen is approximately 1·2–1·8 times that of nitric oxide—namely, 26,000–39,000 cals. per mol., while I. Langmuir, and A. Eucken have shown that the heat of dissociation of nitrogen into atoms is greater than 190,000 cals. and probably of the order of 300,000 or 400,000 cals. per mol. The destruction of the after-glow by a second weak discharge observed by R. J. Strutt also suggests the deactivation of metastable mols. by electrons. A. Fowler and R. J. Strutt's observations (i) that no after-glow occurs when the discharge is such as to give only the line spectrum when nitrogen atoms are definitely present, and (ii) the absence of lines in the after-glow spectrum which would indicate the presence of atoms are not in agreement with the atomic hypothesis of activation, although M. Duffieux and others have shown that free atoms may give rise to band spectra. R. T. Birge favours the atomic hypothesis, but was formerly of the opinion that the α-bands of the after-glow spectra at least are due to metastable nitrogen mols.

at an energy level of 11·5 volts (9·3 volts electronic and 2·2 oscillatory), and that the β- and probably the γ-bands also are due to the presence of small traces of oxygen, perhaps in the form of excited nitric oxide—a view supported by the experiments of R. J. Strutt, and R. S. Mulliken. E. J. B. Willey and E. K. Rideal cited the above arguments, and showed that while the atomic hypothesis requires that the activation of nitrogen requires energy of the order of 300,000 cals. per mol activated nitrogen has a much smaller energy content, and they favour the hypothesis that active nitrogen consists of metastable molecules excited to a level of about 2·0 volts (43,800–41,000 cals.), a value comparable with the "oscillatory" energy of 2·2 volts (50,400 cals.) postulated by R. T. Birge. This relatively low energy content of active nitrogen is said to be consonant with the chemical reactivity of the gas, and may provide an explanation for the excitation of nitrogen in low voltage arcs observed by O. S. Duffendack and K. T. Compton. R. C. Johnson considers that the argument that activated nitrogen consists of metastable molecules with an energy about 42,500 cals. per mol, is not readily reconciled with spectroscopic data for the formation and decomposition of a quasi-stable molecule—*e.g.* N_2I_2, cannot account for the excitation of the 5061-iodine line, and activated nitric oxide molecules cannot account for the spectra which active nitrogen can excite. He therefore prefers the atomic hypothesis.

M. Trautz argued that the dominant constituent of activated nitrogen is triatomic nitrogen, **nitrozone**, or **triazone**, N_3, probably with an open chain structure, because nitrides, not azides, are formed—*vide infra*, mercuric nitride. On cooling, triatomic nitrogen reacts with monatomic nitrogen, forming ordinary nitrogen, N_2; and on heating, triatomic nitrogen forms monatomic and hexatomic nitrogen, N_6, which is present in the gas in very small quantities at low temp. The failure of all attempts to condense any form of active nitrogen led R. J. Strutt to conclude that the formation of triazone is not the cause of the activity. Ozone can be condensed from ozonized oxygen, but not nitrozone from activated nitrogen. However, J. J. Thomson's positive ray analysis (**4.** 25, 9) did reveal the presence of H_3-mols. when the gas is bombarded by anode rays. An active modification of nitrogen, possibly N_3, different from R. J. Strutt's form, was reported by F. L. Usher and R. Venkateswaran to be formed during the electrolysis of soln. of sodium azide, and a similar form, stated to attack mercury, was said by A. W. Browne and G. E. F. Lundell to be evolved at the anode during the electrolysis of soln. of potassium azide in hydrazoic acid at —78°. F. H. Newman found that the α-rays from polonium convert nitrogen into an active form thought to be a mixture of neutral atoms and triatomic mols. If the gas be in the presence of sodium, potassium, phosphorus, sulphur, iodine, magnesium, arsenic, mercury, or a sodium-potassium alloy, some gas is absorbed and in some cases nitrides are formed. G. L. Wendt considered that the failure of the test for nitrides with sulphur, phosphorus, and iodine is not evidence of the absence of chemical reaction. A. Eucken's allotropic α- and β-forms of nitrogen have been discussed in connection with the sp. ht. of nitrogen.

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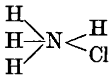
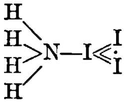
§ 10. The Valency of Nitrogen

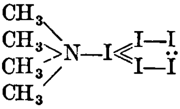
F. A. Kekulé[1] argued that nitrogen is tervalent because in the simplest hydride of nitrogen—ammonia, NH_3—the nitrogen atom behaves as if it were tervalent ; he believed that in ammonium chloride, NH_4Cl, the nitrogen atom is still tervalent if it be assumed that this salt is what he called a mol. compound. This hypothesis was supported by the vapour density observations of H. St. C. Deville and L. Troost, K. von Than, and L. von Pebal, in which the molecule was apparently dissociated : $NH_4Cl \rightarrow HCl + NH_3$. On the other hand, H. B. Baker, and F. M. G. Johnson found that, if thoroughly dried, ammonium chloride can be vaporized without dissociation occurring at all (**2**. 20, 16). This is in agreement with the quinquevalency of nitrogen. Graphically



The same argument, however, would make the nitrogen atom septavalent in R. Abegg and A. Hamburger's NH_4I_3, and nonavalent in C. Weltzien's $N(CH_3)_4I_5$.

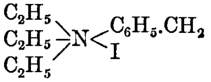
In these cases, however, it is assumed that the halogen may have a greater valency than unity, so that the nitrogen atom still remains quinquevalent:





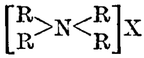
This subject has been discussed by B. Rathke, A. Walter, F. W. Hinrichsen, J. C. Cain, etc.—*vide infra*, ammonium theory. V. Meyer and M. T. Lecco applied an ingenious experiment to test whether nitrogen be ter- or quinquevalent in the ammonium salts. It is agreed that it is tervalent in ammonia, NH_3. Then, like ammonia, (i) the alkyl amines combine directly with acids to form compounds resembling the ammonium salts, *e.g.* trimethylamine unites directly with hydrogen chloride to form trimethylammonium chloride: $N(CH_3)_3+HCl=NH(CH_3)_3Cl$; and (ii) the amines combine with methyl or ethyl iodides, etc., to form corresponding compounds. *E.g.* trimethylamine unites with ethyl iodide: $N(CH_3)_3+C_2H_5I=N(CH_3)_3C_2H_5I$. The properties of the compound $N(CH_3)_3C_2H_5I$ formed by the union of $N(CH_3)_3$ with C_2H_5I are identical with the compound $N(CH_3)_2C_2H_5.CH_3I$ formed by the union of $N(CH_3)_2C_2H_5$ with CH_3I. Consequently, it is inferred that the two compounds must have the same constitution; and that **the ammonium salts cannot be molecular compounds as postulated by F. A. Kekulé,** and that **the nitrogen in ammonium compounds is not tervalent but rather quinquevalent.** The argument is not quite sound, because, as W. Lossen showed, it is possible that the groups are rearranged during the formation of the compounds by the different processes, so that *the* most stable configuration is always formed; and one final product is obtained by the two different reactions. That the question is not definitely closed is illustrated by A. Werner's hypothesis for ammonium chloride H_3N . . . HCl, where the dotted line denotes an auxiliary valence with the nitrogen quadrivalent. There is nothing to show that one of the four hydrogen atoms of this salt is oriented differently from the other three. It will be observed that with quinquevalent nitrogen there is always at least one valency occupied by a group different from the others. According to W. Vaubel, and A. Lachmann, no compound is known with all five valencies occupied by similar radicles. When oxygen exerts its higher valencies, an analogous observation has been made with respect to it. Hence, it is assumed by L. Spicgel that after the three chief valencies of nitrogen are saturated, say with hydrogen, the remaining pair involve the separation of positive and negative charges, an hypothesis which can be formulated, $\ominus-NH_3-\oplus$.

The three valencies of tervalent nitrogen are supposed to lie in one plane since attempts by V. Meyer, A. Ladenburg, E. Fischer, R. Behrend and E. König, F. Krafft, A. Reychler, F. S. Kipping and A. H. Salway, and H. O. Jones and J. P. Millington to prepare optically active derivatives have not been successful. On the other hand, J. A. le Bel, W. J. Pope and co-workers, M. B. Thomas and H. O. Jones, F. W. Fröhlich, E. Wedekind, and H. O. Jones have reported optically active derivatives of quinquevalent nitrogen—*e.g.* lævo- and dextro- α-benzoylphenylallylmethylammonium iodide; other examples are given by M. Scholtz. This is taken to mean that the fourth and fifth valencies of nitrogen are in a plane different from the other three. The experiment of V. Meyer and M. T. Lecco, cited above, is also taken to demonstrate the equivalency of the four valencies of quinquevalent nitrogen to which the alkyl groups are attached—subject, of course, to the limitation indicated by W. Lossen. Some of the alleged isomers are possibly simple cases of dimorphism. S. B. Schryvcr isolated two platinum salts of methyl-diethyl-isoamyl-ammonium chloride; and A. Ladenburg obtained two different triethylbenzylammonium iodides. The one salt is produced by the action of benzyl chloride on triethylamine followed by treatment with iodine; this compound readily parts with benzyl iodide when treated with hydriodic acid, and is supposed to be constituted $(C_2H_5)_3N{=}I(C_6H_5.CH_2)$. The other salt is formed by treating diethylbenzylamine with ethyl iodide; it does not yield benzyl iodide when treated with hydriodic acid; and it is supposed to be constituted:

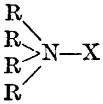


$$\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}>N<\begin{matrix}C_6H_5.CH_2\\I\end{matrix}$$

A spatial or three-dimensional formula for nitrogen, analogous to the carbon tetrahedron, is not possible because there is no symmetrical solid figure with five corners. Hence it was assumed that certain valencies of the nitrogen atom are directed in special directions. Thus were obtained J. H. van't Hoff's cubic or tetrahedral formula, C. Willgerodt's double tetrahedron, C. A. Bischoff's square pyramid, and the modifications suggested by W. Vaubel, and A. von Baeyer. The tetrahedral and the pyramidal or square formulæ can be graphically symbolized:



$$\left[\begin{matrix}R\\R\end{matrix}>N<\begin{matrix}R\\R\end{matrix}\right]X$$



$$\begin{matrix}R\\R\\R\\R\end{matrix}>N-X$$

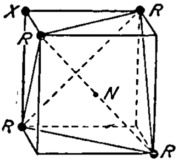


FIG. 9.—Tetrahedron Formula.

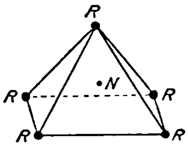
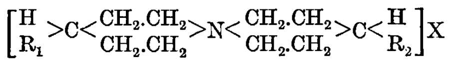


FIG. 10.—Pyramidal Formula.

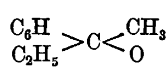
J. C. Cain's idea is that the group ≡N—Cl— acts at the centre of a tetrahedron like the group ≡C—. J. H. van't Hoff assumed that three of the five valencies are alike, while the other two are different because they are active only in special cases. He imagined the nitrogen as being inside a cube with its valencies directed towards five of these corners. By suitably selecting the position of the point representing the nitrogen atom, three of the valencies may be made equal in value, and the remaining two different from themselves and from the others. Analogous modes of representation were employed by A. Béhal, R. Behrend, G. J. Burch and J. E. Marsh, and C. Willgerodt. According to H. O. Jones, if one of the two valencies of the nitrogen atoms were predestined, so to speak, for an alkyl group, and the other for a negative radicle, then only one of the two optical isomers could be produced; but experience shows that the α- and β-forms are produced in equal proportions. Hence, it is assumed that while the three valencies of tervalent nitrogen may lie in one plane, the evocation of two more valencies produces a definite rearrangement whereby two compounds may be formed related to one another in form as object and its mirror image.

The X-radiogram of ammonium chloride by R. W. G. Wyckoff shows that the ammonium radicle persists as an independent entity in the crystalline state, for the crystals of that salt consist of aggregates of alternating ammonium and chloride radicles. H. O. Jones and J. G. M. Dunlop favoured the pyramidal formula; but W. H. Mills and E. H. Warren obtained salts of the type:



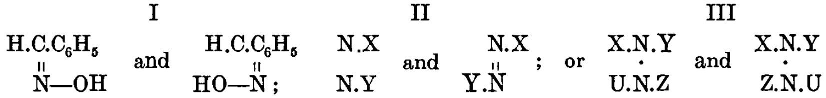
$$\left[\begin{matrix}H\\R_1\end{matrix}>C<\begin{matrix}CH_2.CH_2\\CH_2.CH_2\end{matrix}>N<\begin{matrix}CH_2.CH_2\\CH_2.CH_2\end{matrix}>C<\begin{matrix}H\\R_2\end{matrix}\right]X$$

which are capable of being resolved into optical isomerides. This is taken to be in harmony with the tetrahedral but not with the pyramidal hypothesis. The stereochemistry of the four radicles of the ammonium ion were thought by A. Werner to be identical with those of methane; and the optically active methylethyl aniline oxide of J. Meisenheimer can be represented as a quadri-covalent compound without embarrassment with respect to the semi-polar double-bonded oxygen:



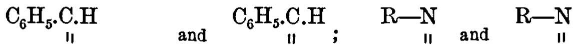
$$\begin{array}{c}C_6H\\C_2H_5\end{array}\!>C<\!\begin{array}{c}CH_3\\O\end{array}$$

A. Hantzsch and A. Werner[2] assumed that in certain compounds the third valency of the tervalent nitrogen atoms does not necessarily lie in the same plane as the other two. This hypothesis, that the three bonds of a doubly-bound atom of nitrogen in the oximes and related compounds are not co-planar, was strengthened by the work of W. H. Mills and A. M. Bain, and W. H. Mills and H. Schindler. T. M. Lowry said that whatever opinion is held as to the asymmetry of the trisubstituted ammonia from which it is derived, the nitrogen atom of the pyrrolidine ring of the nicotinium ion must be regarded as asymmetric, a deduction which receives support from the fact that nicotine acetate has $[\alpha]_D=+18{\cdot}85°$, whilst nicotine has $[\alpha]_D=-169°$. The anomaly is not observed in cases where the formation of a salt is unaccompanied by fundamental change in the character of the asymmetric system. A. E. Uspensky discussed the spatial distribution of the valency directions of tervalent nitrogen. In certain compounds, the three valencies of the nitrogen atom act towards the corners of a, not necessarily regular, tetrahedron, in whose fourth corner, the nitrogen atom is itself situated. This may give three cases of isomerism:



$$\begin{array}{cccccccccc} & \text{I} & & & \text{II} & & & & \text{III} & \\ H.C.C_6H_5 & & H.C.C_6H_5 & N.X & & N.X & & X.N.Y & & X.N.Y\\ \| & \text{and} & \| & & \text{and} & \| & ;\ \text{or} & \cdot & \text{and} & \cdot \\ N{-}OH & & HO{-}N; & N.Y & & Y.N & & U.N.Z & & Z.N.U\end{array}$$

The hypothesis was discussed by K. Auwers and V. Meyer, H. Goldschmidt, E. Müller, A. Hantzsch, E. Beckmann, etc. In order to distinguish between these isomeric forms of, say, the benzaldoximes, A. Hantzsch employs the term **syn** as a prefix to indicate that the hydroxyl group lies on the same side of the mol. as the hydrogen atom of the aldehyde, and **anti** when the hydrogen and hydroxyl lie on opposite sides of the mol. The same nomenclature is applied to other compounds, *e.g.* the potassium benzoylphenyldiazotates, etc. Thus:

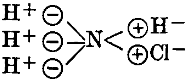


$$\begin{array}{ccccccc} C_6H_5.C.H & & C_6H_5.C.H & & R{-}N & & R{-}N\\ \| & \text{and} & \| & ; & \| & \text{and} & \| \\ N{-}OH & & HO{-}N & & KO{-}N & & N{-}OK\end{array}$$

Syn-aldoxime. *Anti*-aldoxime. *Syn*-diazotate. *Anti*-diazotate.

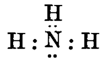
This subject is discussed in special memoirs: E. Wedekind, *Die Entwicklung der Stereochemie des funfwertigen Stickstoffs im letzten Jahrzehnt*, Stuttgart, 1909; *Stereochemie*, Leipzig, 1904; J. H. van't Hoff, *The Arrangement of Atoms in Space*, London, 1898; *La chimie dans l'espace*, Rotterdam, 1875; Oxford, 1891; A. W. Stewart, *Stereochemistry*, London, 1919; J. N. Friend, *The Theory of Valency*, London, 1915; H. Kaufmann, *Die Valenzlehre*, Stuttgart, 1911; A. Eiloart, *A Guide to Stereochemistry*, New York, 1893; C. A. Bischoff and P. Walden, *Handbuch der Stereochemie*, Frankfurt, 1894; C. A. Bischoff, *Materialen der Stereochemie*, Braunschweig, 1904; L. Mamlock, *Stereochemie*, Leipzig, 1907; P. Freundler, *La Stéréochimie*, Paris, 1899; P. Bruylants, *La valence chimique*, Louvain, 1912; K. Auwers, *Die Entwicklung der Stereochemie*, Heidelberg, 1890; W. Meyerhoffer, *Stereochemie*, Leipzig, 1892; E. G. Mond, *Stéréochimie*, Paris, 1895; A. Hantzsch, *Grundriss der Stereochemie*, Breslau, 1893; W. van Ryn, *Die Stereochemie der Stickstoffs*, Zürich, 1897; W. Vaubel, *Stereochemische Forschungen*, München, 1899.

According to R. Abegg's theory[3] of co-valency (**4.** 27, 3), nitrogen has three negative and five positive valencies. The positive valencies are illustrated by the oxides and halides; whereas in ammonia, the three negative valencies of nitrogen are saturated. In ammonium chloride, the positive and negative valencies are represented by the scheme:

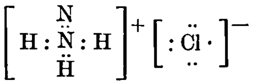


$$\begin{array}{l}H^+\ominus\\H^+\ominus\\H^+\ominus\end{array}\!>N<\!\begin{array}{l}\oplus H^-\\\oplus Cl^-\end{array}$$

The attachment of the fourth hydrogen atom by a weak positive or contra-valency is supposed to explain the ready dissociation of that salt on heating. J. N. Friend, and F. Wenzel have described a modification of this hypothesis. F. Wenzel attempted to account for the behaviour of nitrogen compounds on the assumption that the valencies of nitrogen are divisible into two distinct groups, one of which includes two and the other three valencies which are equal in all respects. When quinquevalent nitrogen is transformed into tervalent nitrogen there is a loss of one valency from each group. This change is supposed to result in the formation of an intra-atomic double linking connecting dissimilar nuclei. In support of this theory attention is directed to the similarity between the amines and ethylene derivatives in respect of their capacity to form additive compounds. F. Wenzel said that there is no satisfactory evidence to support the view that four of the nitrogen valencies bear the same relation to the fifth. Whilst certain chemical observations suggest that there are two pairs of valencies which are identical in relation to the fifth valency, physico-chemical data indicate that there are three valencies which are identical with regard to the fifth valency. From this it is inferred that the fifth valency does not always represent one and the same valency unit. R. De, and J. Picard and J. H. Dardel discussed the valency of nitrogen from the point of view of the co-ordination theory. The electronic structure of ammonia, and ammonium chloride can be represented:



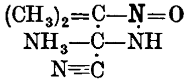
$$\begin{array}{c}\mathrm{H}\\ \mathrm{H}:\underset{\cdot\cdot}{\ddot{\mathrm{N}}}:\mathrm{H}\end{array}$$



$$\left[\begin{array}{c}\mathrm{N}\\ \mathrm{H}:\ddot{\mathrm{N}}:\mathrm{H}\\ \ddot{\mathrm{H}}\end{array}\right]^{+}\left[:\underset{\cdot\cdot}{\ddot{\mathrm{Cl}}}\cdot\right]^{-}$$

and this fits in with the hypothesis of A. Werner and with that of J. H. van't Hoff —*vide supra*—namely, that *the four positive radicles of the ammonium salts are tetrahedrally disposed.* A. A. Blanchard added that nitrogen can have but eight and hydrogen but two electrons in its valency shell although phosphorus may have more than eight. Defining the non-polar valency as the number of pairs held in common with other atoms, nitrogen can have a maximum non-polar valency of four. The polar valency may be regarded as plus five if we define it as the net charge of the nitrogen kernel, or as minus three if we define it as the charge of the nitrogen atom and consider the eight electrons of the shell as a part of the atom. The subject was discussed by J. H. W. Booth, and E. Müller.

In nitric oxide, the nitrogen atom behaves as if it were *bivalent* or *quadrivalent.* The latter is assumed because the mols. of nitric oxide, NO, do not associate at temp. as low as —100°. If association did occur, it would be attributed to the activity of either the oxygen, $N{=}O{=}O{=}N$, or the nitrogen, $O{=}N{=}N{=}O$. The unsaturated nature of the nitric oxide mol. is shown by its immediate formation of nitrogen peroxide, N_2O_4, in the presence of free oxygen. The rupture of the oxygen mol. during this reaction is shown by the fact that when heated, the nitrogen peroxide does not dissociate into nitric oxide and oxygen, but into single mols.: $N_2O_4 \rightleftharpoons 2NO_2$. F. Raschig's[4] idea that potassium peroxylaminesulphonic acid, $(KO.SO_2)_2{=}N{=}O$, contains quadrivalent nitrogen was questioned by T. Haga, who doubled the formula so as to furnish $(KO.SO_2)_2{=}N{-}O{-}O{-}N{=}(KO.SO_2)_2$. O. Piloty and B. Schwerin stated that the porphyrexine which they prepared contained quadrivalent nitrogen, say:



$$\begin{array}{rcl}(\mathrm{CH_3})_2{=}&\underset{\cdot}{\mathrm{C}}&{-}\underset{\cdot}{\mathbf{N}}{=}\mathrm{O}\\ \mathrm{NH_3}{-}&\underset{\cdot}{\mathrm{C}}&{-}\mathrm{NH}\\ \mathrm{N}{\equiv}&\mathrm{C}&\end{array}$$

but the hypothesis has not been confirmed. F. H. Banfield and J. Kenyon prepared oxidation products of a substituted hydroxylamine which they supposed to contain quadrivalent nitrogen: $R_2{=}N{-}OH \rightarrow R_2{=}N{=}O$; but T. M. Lowry showed that the reaction can be explained by assuming the nitrogen tervalent throughout. C. W. Blomstrand, F. Barker, and A. P. Mathews also put forward the hypothesis that nitrogen can act as a *univalent* element. There is no satisfactory evidence to support this assumption.

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§ 11. The Atomic Weight of Nitrogen

According to H. E. Roscoe and A. Harden,[1] J. Dalton first deduced the value 4 for the eq. weight of nitrogen from an old analysis of ammonia by W. Austin, and later from the analysis of ammonia by C. L. Berthollet, and of nitrogen oxide by H. Davy ; he gave 5 for the at. wt. of nitrogen. In 1811, J. J. Berzelius analyzed ammonium chloride and obtained 14·22–14·66 for the at. wt. of nitrogen. In 1820,

J. J. Berzelius and P. L. Dulong showed that the vap. density of nitrogen gas is in agreement with the views of L. Gmelin, W. Prout, and J. J. G. Meinecke, who gave 14 for the at. wt. of nitrogen. L. Gmelin obtained 14·08 from the ratio Ag : $AgNO_3$; F. Penny, 13·98–13·99; J. C. G. de Marignac, 13·99–14·005; J. S. Stas, 14·00–14·049; W. L. Hardin, 14·015–14·037; and T. W. Richards and G. S. Forbes, 14·008–14·031 with Ag=107·880–107·92. J. C. G. de Marignac obtained 13·98 from the ratio Ag : NH_4Cl; J. Pelouze, 13·96; J. S. Stas, 14·014–14·027; and A. Scott, 14·007–14·111. J. S. Stas obtained 14·042–14·045 from the ratio Ag : NH_4Br; and A. Scott, 14·005–14·011. E. Turner obtained 14·01–14·03 from the ratio $AgNO_3$: AgCl, and F. Penny, 14·01–14·025. A. Scott obtained 14·014–14·017 from the ratio NH_4Cl : AgCl. J. C. G. de Marignac calculated 14·07–14·08 from the ratio KCl : $AgNO_3$; and J. S. Stas, 14·05–14·06; J. S. Stas obtained 14·003–14·006 from the ratio $AgNO_3$: NH_4Cl. G. Dean calculated 14·02–14·03 from the ratio KBr : AgCy. L. F. Svanberg calculated 13·91 from the ratio $Pb(NO_3)_2$: PbO. F. Penny obtained 14·05 from the ratio KCl : KNO_3; J. S. Stas, 14·04–14·05; and J. G. Hibbs, 14·03–14·04. F. Penny obtained 14·02–14·03 from the ratio NaCl : $NaNO_3$; J. S. Stas, 14·04–14·05; and J. G. Hibbs, 14·010–14·022. F. Penny obtained 14·02 from the ratio $KClO_3$: KNO_3, and 14·05 from the ratio $NaClO_3$: $NaNO_3$. J. Thomsen obtained 14·024–14·028 from the ratio NH_3 : HCl; and T. W. Richards and E. H. Archibald, 13·992–14·005 from the ratio $2KNO_3$: K_2O, and 14·004–14·018 from the ratio $2CsNO_3$: Cs_2O. From the gas analyses of P. A. Guye and co-workers, they calculated 14·007 from the ratio N_2O : O, and 14·010 from the ratio N_2 : O; A. Jaquerod and S. Bogdan, 14·015 from the ratio N_2O : N_2; and R. W. Gray, 14·009–14·011 from the ratio NO : N, and 14·009 from the ratio N : O.

From the density determinations of A. Leduc, D. Berthelot, P. A. Guye and L. Friderich, Lord Rayleigh, A. Jaquerod and F. L. Perrot, and R. W. Gray, the value 14·009 is derived from the ratio N_2 : O_2 for the at. wt. of nitrogen; D. Berthelot, Lord Rayleigh, A. Leduc, and P. A. Guye, 14·006 from the ratio N_2 : CO; A. Leduc, Lord Rayleigh, and P. A. Guye and A. Pintza, 14·007 from the ratio N_2O : CO_2; P. A. Guye, and P. A. Guye and A. Pintza, Lord Rayleigh, and A. Leduc, 14·006 from the ratio N_2O : O_2; A. Jaquerod and O. Scheuer, P. A. Guye, and R. W. Gray, 14·008 from the ratio NO : O_2; P. A. Guye and A. Pintza, and E. P. Perman and J. H. Davies, 14·010 from the ratio NH_3 : O_2; H. V. Regnault obtained 14·056, H unity; and M. Vezes, 14·040, oxygen 16. By the method of limiting densities, D. Berthelot obtained 14·007 from N_2, 13·997 from N_2O, hydrogen 1·0077. A. Leduc obtained 14·008 by the method of corresponding vol.; T. Bateiecas, 14·005; G. P. Baxter and H. W. Starkweather, 14·007; and G. M. Maverick, 13·996 from compressibility data; and P. A. Guye, 14·007, by the method of critical constants. By considering all the data, F. W. Clarke derived 14·0101, oxygen 16; G. D. Hinrichs, 14 ± 0·001, oxygen 16; B. Brauner, 14·010; J. D. van der Plaats, 14·0421; W. Ostwald, 14·0410; and E. Moles and J. M. Clavera, 14·008. The International Table of Atomic Weights (1924) gave 14·01 for the at. wt. of nitrogen—oxygen 16.

The **atomic number** of nitrogen is 7. F. W. Aston[2] found no **isotopes,** there being only one form of atom of mass 14; J. L. Costa obtained a value greater than 14 and less than 14·008; E. Rutherford and J. Chadwick reported that they had succeeded in the **disintegration of the nitrogen atom.** They bombarded nitrogen gas with α-particles derived from radium-C, and obtained long-range particles of hydrogen nuclei which are assumed to have been knocked away from the nitrogen atoms during the collision. About one impact of the α-particles with the nitrogen atom out of twelve succeeds in breaking up the atom. The subject was discussed by E. Chalfin, G. Kirsch and H. Pettersson, R. W. Millar, G. Kirsch, W. Lenz, V. Kondratjeff, H. T. Wolff, P. S. M. Blackett, W. D. Harkins and H. A. Shadduck, and A. Smekal. For the transmutation of nitrogen into helium, hydrogen, and neon, by R. W. Riding and E. C. C. Baly, *vide* **7.** 48, 6. A. L. Foley studied the effect on the spectra of the exposure of nitrogen, confined in sealed glass tubes, to ultra-violet light, and to the X-rays, but with no definite results.

According to N. Bohr, the **electronic structure** of the atom of nitrogen is as follows: There are two electrons in the first ring about the central nucleus or proton, four in the second, and one in the third or outer ring: (2) (4, 1). From the general similarity in the physical properties of carbon monoxide and nitrogen, I. Langmuir inferred that there is a resemblance in the electronic structure of the two mols. (**4**. 27, 4). P. D. Foote suggested that the presence of occluded nitrogen in uraninite shows that the atom of uranium possibly contains nitrogen nuclei. H. G. Grimm and A. Sommerfeld, F. P. Worley, W. A. Wahl, H. Nagaoka, I. S. Bowen and R. A. Millikan, J. C. McLennan and co-workers, P. M. S. Blackett, R. A. Birge, J. H. Jones, I. Woodward, J. R. Partington, A. O. Rankine, K. R. Ramanathan, G. Kirsch, H. Collins, H. Burgarth, A. W. C. Menzies, H. Lessheim and R. Samuel, E. C. Stoner, G. P. Thomson and R. G. J. Frazer, C. D. Niven, M. L. Huggins, etc., studied the electronic structure.

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§ 12. The Nitrides

The metals lithium, magnesium, boron, and aluminium form a mixture of oxides and nitrides when oxidized in air; and the elements lithium, calcium, strontium, barium, magnesium, boron, aluminium, the rare earth metals, silicon, titanium, zirconium, cerium, thorium, vanadium, columbium, tantalum, chromium, uranium, and manganese form **nitrides** when heated in an atm. of nitrogen. Instead of the metal, the amalgam can be used as with Ca, Ba, and Mn; a mixture of the metal oxide and carbon—B, Al, Si, and Mg; a mixture of the metal oxide and carbon—Bi, Si, Ti, Mg, and V; a mixture of the metal oxide and magnesium or aluminium—Ce, La, Nd, Pr, and U; the metal carbide—Ba, Sr, and Ca (cyanides may be formed); or the metal hydride—Bi, Si, Ti, Ca, Ba, Sr, Mg, and V. Nitrides have also been made by the action of activated nitrogen on the metal. The nitrides can also be produced by heating many metals in ammonia—K, Cu, Ba, Mg, Zn, Cd, B, Al, Ti, Th, Cr, Mo, Mn, Fe, Co, and Ni. Instead of the metal, the amalgam can be used—Fe and Mn; the metal oxide—Cu, Hg, B, Ti, and Cb; the metal carbide—Th; the metal chloride—Si, Ti, Zr, Th, Cr, Mo, W, U, Cb, Ta, V, and Fe; the metal bromide or iodide—Bi, and Fe; and the metal nitrate—Cu (and liquid ammonia). The nitrides are also produced by heating the metal and calcium carbide in air—Zn, Al, and Fe; the metal and aluminium in air—Zr; the metal and lime in air—Al; the metal and soda or carbon in air—Al; the metal oxide and carbon in air—Ti, and B; the metal oxide and magnesium in air—Ca, Sr, Ba, Al, and Zr; the metal and nitrogen trioxide—Bi. The nitrides may also be formed by the decomposition of an amide or imide—K, Ba, Cu, Cd, Zn, and B; by the action of cyanides or by heating the metal in cyanogen;[1] and by double decomposition with other nitrides—*e.g.* copper oxide and magnesium nitride give copper nitride.

In the normal nitrides, nitrogen is tervalent so that the general formula of the nitrides of the univalent elements is R_3N; of the bivalent elements, R_3N_2; of the tervalent elements, RN; of the quadrivalent elements, R_3N_4; and of the quinquevalent elements, R_3N_5. The compounds of the metals with the univalent radicle, N_3, are salts of hydrazoic acid, HN_3, and are called azides—*vide infra.* The relationship of the nitrides to ammonia is shown by the evolution of ammonia when the soluble nitrides are treated with water, an acid, or alkali-lye; or when the insoluble nitrides are fused with alkali hydroxide. Usually the nitride is decomposed by steam giving off ammonia; but in the case of cerium nitride, some hydrogen is simultaneously formed. When the nitrides are oxidized, free nitrogen is evolved and an oxide of the metal is formed. Only in the case of boron nitride is some nitrogen simultaneously oxidized.

Among the alkali metals, lithium is exceptional in readily combining directly with nitrogen, but sodium, potassium, rubidium, and cæsium do not form nitrides when heated in nitrogen under ordinary conditions. H. Deslandres[2] found that the combination with lithium occurs even at ordinary temp. L. Ouvrard prepared **lithium nitride**, Li_3N, by heating gradually to dull redness lithium contained in an iron boat in a current of nitrogen. The metal becomes incandescent and the nitride is formed. A. Guntz found the product so obtained was contaminated with 2–8 per cent. of iron, but the result was no better if a vessel of nickel, quartz, or carbon be employed; silver, and platinum are dissolved by molten lithium. F. W. Dafert and R. Miklauz said that the lithium unites with pure dry nitrogen even at ordinary temp., forming the nitride; the presence of relatively small proportions of oxygen or hydrogen completely prevents the reaction so that lithium is not attacked by dry air at room-temp. W. Frankenburger measured the velocity of formation of lithium nitride from the metal and nitrogen between —55° and —30°, and found it to be proportional to the surface of the formed nitride $-dp/dt=KM^{\frac{2}{3}}$. He also found that $k=CT^{\frac{1}{2}}e-Q/RT$; and that the increase in the velocity with temp. depends on the increase in the fraction, $e-Q/RT$, of the total number of collisions which take place between the lithium surface and the N_2-molecules. This gives the number of collisions possessing an energy $Q=16{\cdot}4$ cals. per mol. At 240° K., this fraction is approximately $1{\cdot}2\times10^{-15}$. The value for C between —55° and —30° is $C=2{\cdot}153\times10^{31}$. The term $CT^{\frac{1}{2}}$ is equal to the number of collisions, S per sec. at $T°$, on the surface of the lithium. The number of collisions for a gas of mol. vol. v is known to be $(N/v)(RT/2\pi M)^{-\frac{1}{2}}$ per sq. cm. per sec.; and with a surface 50 sq. cm. $ST^{-\frac{1}{2}}=1{\cdot}01\times10^{24}$. This, taken in conjunction with C, shows that the velocity of the reaction is greater by the fraction 21×10^6 than would be the case if only the collisions with a heat of activation of 16·4 cals. were chemically fruitful. C. Urfer prepared lithium nitride by heating an amalgam to about 600° in an atm. of nitrogen. Lithium nitride furnishes a spongy black mass which is readily attacked by water, forming ammonia and lithium hydroxide. W. Frankenburger found that the X-radiogram shows that the crystals of lithium nitride belong to the cubic system; that the space-lattice has a side of 5·5 A., and that each cell has 4 atoms of nitrogen, and 12 atoms of lithium. R. Brill also examined the space lattice of lithium nitride, and found it to be analogous to that of ammonia, NH_3. F. W. Dafert and R. Miklauz found that lithium nitride melts at 840°–845°. A. Guntz gave for the heat of soln., 131·1 Cals.; and for the heat of formation: $3Li_{solid}+N_{gas}=Li_3N_{solid}+49{\cdot}5$ Cals.; A. Guntz and F. Benoit gave 33 Cals. Lithium nitride gives the hydride when heated in a current of hydrogen: *e.g.* $Li_3N+3H_2=NH_3+3LiH$. According to A. Guntz, lithium nitride reacts with a large number of the metal chlorides, MCl, forming the metal nitride: $Li_3N+3MCl=M_3N+3LiCl$. The thermal value of the reaction is usually high because lithium chloride is formed with rather a large evolution of heat. F. W. Dafert and R. Miklauz said that the fused nitride rapidly attacks iron, nickel, copper, platinum, porcelain, and other silicates. At 870°, it will eat through any known containing vessel. It penetrates through magnesia vessels as through a filter. For the products formed by the action of hydrogen, *vide infra*, lithium amide and imide. A. Remelé observed the photoelectric effect with lithium nitride. L. Zehnder said that **sodium nitride**, Na_3N, is formed when metallic sodium is made the cathode for an electric discharge in nitrogen gas. The black product collects on the walls of the tube in the vicinity of the anode. When heated, the nitride is said to decompose into nitrogen and sodium; and to be decomposed by water with the evolution of nitrogen, but G. Salet showed that the gas given off is ammonia. H. Hardtung was unsuccessful in an attempt to make the nitride by heating sodium at 250°–400° in dry nitrogen. J. L. Gay Lussac and L. J. Thénard reported that a black nitride is formed when sodamide is heated, but A. W. Titherley was unable to confirm this. F. Fischer and F. Schröter prepared sodium nitride mixed with free sodium, in the apparatus illustrated diagrammatically in Fig. 11. A glass tube, *A*, contains a platinum cathode, *B*, fused into the glass. The movable anode, *C*, is made of the metal whose nitride is desired. The gap between anode and cathode is regulated by rotating the stopper *D* which is fitted with a screw-thread as shown. The stopper is sealed by the mercury in the cup *S*. The side-tubes *F* and *G* are used for collecting the nitride formed in the lower part of the tube. Liquid nitrogen is placed in the lower part of *A*, an arc is established, and the vap. of the required element and nitrogen is raised locally to a high temp., and then quickly cooled by the excess of liquid surrounding the arc. A mixture of nitrogen with nine times its vol. of argon was employed; this increases the rate of disintegration of the metal electrode. The resulting black sodium nitride when heated gives off nitrogen with explosive violence; and it dissolves in water with the evolution of ammonia. J. L. Gay Lussac and L. J. Thénard reported **potassium nitride,** K_3N, to be formed, as a greenish-black, infusible mass, by heating potassium amide to redness in a closed vessel. A. W. Titherley was unable to verify this with the amide he prepared; but H. Davy confirmed J. L. Gay Lussac and L. J. Thénard's observation, and added that a black product is formed at a higher temp. It is decomposed at a high temp. into its elements; it generally takes fire spontaneously in air, burning with a dark red flame. It gives off nitrogen when burnt in oxygen, or when heated with mercuric oxide. It effervesces violently with water with the evolution of ammonia: $K_3N+3H_2O=3KOH+NH_3$. It unites with phosphorus or sulphur when heated, forming a highly inflammable mixture, which, coming in contact with water, evolves ammonia and phosphine or hydrogen sulphide. F. Fischer and F. Schröter obtained it as a blue compound by the method illustrated in Fig. 11. The product resembled sodium nitride in its chemical properties. H. Moissan prepared **rubidium nitride,** Rb_3N, by heating rubidium hydride in a current of nitrogen—some rubidium amide is formed at the same time. F. Fischer and F. Schröter prepared rubidium nitride as a blue compound by the method depicted in Fig. 11. H. Moissan reported **cæsium nitride,** Cs_3N, to be formed by the method he employed for rubidium nitride. The alkali nitrides burn in air, and they are readily attacked by chlorine, phosphorus, and sulphur; water decomposes them quantitatively into the metal hydroxide and ammonia; and dil. acids give ammonia and the corresponding salt. R. Suhrmann and K. Clusius observed that the m.p. of potassium nitride is 343° and its decomposition temp. 355°; rubidium nitride melts at 321° and decomposes at 395°; cæsium nitride melts at 326° and decomposes at 390°; while sodium nitride decomposes at 275° below its m.p.

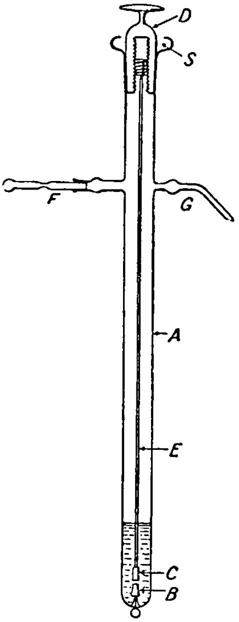


FIG. 11.—Apparatus for making Nitrides.

P. L. Aslanoglou[3] found that powdered copper heated in an atmosphere of nitrogen does not form a nitride; and K. Iwase, and I. I. Shukoff observed no absorption of nitrogen by the metal at 1250°. G. Tammann, however, said that a nitride is formed. K. Iwase found nitrogen is absorbed by liquid copper. The observations of L. J. Thénard, F. Savart, C. Despretz, R. Blondlot, H. N. Warren, C. Matignon and R. Trannoy, C. H. Pfaff, C. W. J. Kastner, W. R. Grove, J. F. Daniell, H. Pauli, A. Rossel, and L. Arons on this subject have been discussed in connection with the action of nitrogen and of ammonia on copper (**1**. 21, 6). According to A. Schrötter, and H. Herzer, **cuprous nitride,** Cu_3N, is produced by the action of ammonia on cupric oxide at, say, 250°, for 120 hrs.: $6CuO+4NH_3=2Cu_3N+6H_2O+N_2$. The rate of formation is therefore very slow. If the temp. is too high, the metal alone is produced. The product is contaminated with free oxide and the metal. Some occluded hydrogen is also present. A. Guntz and H. Bassett recommended using copper oxide freed from chloride and dried at 130°; they also said that no more than three grams should be made in one operation. G. T. Beilby and G. G. Henderson said that no nitride is formed unless the ammonia is present in large excess. J. J. Berzelius extracted cuprous oxide with a mixture of aq. ammonia and ammonium carbonate; in this way A. Guntz and H. Bassett transformed a sample with 83·82 per cent. nitride into one with 93 per cent. nitride. These workers also recommended using cuprous oxide in place of cupric oxide. Crystalline cuprous oxide acts more slowly than the precipitated oxide. They treated precipitated and dried cuprous oxide at 265° for two hours. They said that the reaction with the crystalline oxide begins at 270° and is very rapid at 310°. The nitride begins to decompose very near its temp. of formation so that the product is not very pure. A. Smits made copper nitride by the interaction of magnesium nitride and copper oxide and sulphate, but the product is very impure. E. B. Maxted tried heating cuprous oxide or chloride with lithium nitride, but the reaction is so violent that the copper nitride is decomposed and copper alone is obtained. According to F. F. Fitzgerald, when potassamide is added to a soln. of copper nitrate in liquid ammonia, an olive-green precipitate is formed, which is possibly $CuNH_2$ or Cu_2NH. When this product is dried in vacuo at 160°, it gives off nitrogen, but not ammonia, and forms cuprous nitride as a black, amorphous mass. A. C. Vournasos made **cupric nitride** by heating copper cyanide with ammonium nitrate: $3Cu(CN)_2+12NH_4NO_3=Cu_3N_2+6CO_2+14N_2+24H_2O$. Cuprous nitride is a very dark green powder which, according to A. Schrötter, is not decomposed by percussion or friction, but is decomposed into its elements when heated in air in the vicinity of 300°; and the reaction is accompanied by a red glow. If it be heated in oxygen decomposition occurs below 300°, and if in nitrogen, or carbon dioxide, above 300°. If the nitride is contaminated with cupric oxide, nitric oxide as well as nitrogen will be given off. A. Guntz and H. Bassett said that in carbon dioxide, the decomposition is complete at 600°; and if heated too rapidly, small explosions occur. J. J. Berzelius said that the nitride purified by the ammoniacal soln. decomposes at a lower temp. and with a slight explosion. F. F. Fitzgerald found that the nitride rapidly explodes when heated in air; and it is decomposed by water with a considerable evolution of heat. According to A. Schrötter, chlorine decomposes the nitride with the evolution of heat, and the formation of cupric chloride—A. Guntz and H. Bassett said cuprous chloride—and nitrogen; and with hydrogen chloride, cuprous and ammonium chlorides are formed. J. J. Berzelius said that with dil. acids, cuprous salts are formed and ammonia is evolved. According to A. Guntz and H. Bassett, the cuprous salt is formed quantitatively: $2Cu_3N+8HCl=6CuCl+2NH_4Cl$. The conc. acid dissolves the nitride rapidly, and the soln. on dilution precipitates cuprous chloride. F. F. Fitzgerald found that the nitride is completely soluble in hydrochloric acid, forming a colourless soln. According to A. Guntz and H. Bassett, if a little conc. sulphuric acid be poured on copper nitride, there is an energetic reaction, copper and cuprous oxide are formed and ammonium sulphate is produced without a loss of nitrogen. F. F. Fitzgerald said that sulphuric acid converts the nitride into an eq. quantity of copper and cupric sulphate. A. Schrötter said that sulphuric acid rapidly liberates nitrogen and leaves metallic copper behind; other non-oxidizing acids act similarly, but more slowly in proportion as they are more dil. Conc. nitric acid oxidizes the nitride with great violence; and, added A. Guntz and H. Bassett, scarcely half the nitrogen is transformed into ammonia; with dil. nitric acid, the action is less vigorous. Soln. of the alkali hydroxides have but a feeble action on the nitride in the cold; and even a boiling conc. soln. of sodium hydroxide requires an hour for a 10 per cent. decomposition: $2Cu_3N+3H_2O=3Cu_2O+2NH_3$.

Observations on *C. L. Berthollet's*[4] *l'argent fulminant* made by M. Faraday, L. A. Crell, B. Higgins, E. Murmann, N. W. Fischer, L. J. Proust, J. L. Gay Lussac, and M. H. Klaproth and F. Wolff have been discussed in connection with silver hydroxide (**3.** 22, 11). G. T. Beilby and G. G. Henderson found that when silver is heated in ammonia the physical structure of the metal is altered, but no nitride is formed. According to F. Raschig, the fulminating silver obtained by the action of aq. ammonia on silver oxide appears to have been **silver nitride,** Ag_3N, mixed with varying proportions of metallic silver. He obtained the product in a fairly pure state by treating silver oxide with 2 c.c. of ammonia in 25 per cent. aq. soln. per gram of oxide. When allowed to stand in the dark for 16–20 hrs., crystals of silver nitride separate out. The silver nitride may be also separated from the soln. by adding to the ammoniacal soln. ten times its vol. of alcohol; or by heating the soln. gently on a water-bath. The nitride is explosive, and it must not be disturbed until cold. The grey precipitate quickly darkens on standing, and it spontaneously decomposes into silver and nitrogen so that specimens usually contain some free silver. The nitride explodes easily and violently—particularly when dry. When treated with hydrochloric acid, the nitride is converted into ammonium and silver chlorides; with nitric acid, the conversion to ammonium and silver nitrates is complete. In the former case, the insolubility of the silver chloride hampers the reaction. Dil. sulphuric acid forms soluble ammonium and silver sulphates. Silver nitride is decomposed by a soln. of potassium cyanide: $Ag_3N+3KCy+3H_2O=NH_3+3KOH+3AgCy$. L. J. Olmer and M. Dervin found that silver ammonium fluoride decomposes below 160°, forming black silver nitride, Ag_3N, which is more unstable towards friction than towards temp. It sometimes explodes spontaneously between 140° and 160° after about 10 minutes, but below 140° it is more stable. It always explodes by contact or by a neighbouring detonation.

Nitrogen has no action on gold. G. T. Beilby and G. G. Henderson observed that no nitride is formed when gold is heated in ammonia, but the physical structure of the metal is much altered. The action of ammonia on gold oxide, resulting in the formation of fulminating gold, has been discussed in connection with gold oxide (**3.** 23, 14). According to W. R. Grove,[5] when water containing ammonium and auric chlorides is electrolyzed with a platinum anode and a gold cathode, a black substance is formed on the cathode. Its sp. gr. is 10·3, and when heated, it gives off 273 c.c. of nitrogen per gram. F. Raschig found that when conc. aq. ammonia is added to water containing aurous oxide in suspension, a black explosive powder, *aurous amminonitride,* $Au_3N.NH_3.(4H_2O)$, is formed; and this, when boiled with water, or dil. acids, furnishes **hemitrihydrated gold nitride,** $Au_3N.1\frac{1}{2}H_2O$. It is not decomposed by dil. nitric acid. If gold aurosoauric oxide be similarly treated, it forms a black *aurous amminotrihydroxynitride,* $Au_3N_2.3H_2O$, or $(AuOH)_3.N.NH_3$, which is very explosive when dry. Warm hydrochloric acid dissolves two-thirds the gold, and leaves one-third in the metallic state. When boiled with water, half the nitrogen is expelled, and **pentahydrated gold nitride,** $Au_3N.5H_2O$, is formed. It is not decomposed by boiling with dil. acetic, nitric, or sulphuric acid.

The metals of the alkaline earths all readily combine with nitrogen at a high temp., forming nitrides. F. W. Dafert and R. Miklauz[6] said that the reactions with calcium, strontium, and barium occur respectively at 410°, 380°, and 260°. According to H. Moissan, calcium is scarcely affected by nitrogen at ordinary temp., but when the temp. is raised a little, the surface of the metal becomes yellow and then bronze coloured. E. Biesalsky and H. van Eck studied the affinity of calcium for nitrogen; and C. Montemartini and L. Losana, the partition of oxygen and nitrogen, dry and moist, with calcium. According to H. Moissan, when calcium in an atm. of nitrogen is heated by a blast gas-flame, it forms a brown partly-sintered mass; it requires two hours' heating in an iron tube to complete the reaction. The product is **calcium nitride,** Ca_3N_2. I. I. Shukoff found the reaction is vigorous at 780° ; H. Herzer, and H. Hardtung worked at 900°. K. Kaiser obtained the nitride by the action of nitrogen on the heated sulphide. O. Ruff showed that calcium, when alloyed with more electropositive metals such as strontium, barium, sodium, or potassium, or with calcium nitride, combines more readily with nitrogen than pure calcium. From this observation it is concluded that the heteropolar nature of a metallic surface favours the combination with a homopolar gas, and from this it is assumed that it acquires influence charges from the surface valencies of the metal which determine its position and behaviour towards the surface. O. Ruff and co-workers added that the rate at which alloys rich in calcium absorb nitrogen depends on vol. relationship, temperature, potential of the added metal, and the calcium nitride content of the alloy. The contraction of calcium in the formation of calcium nitride keeps the exposed surface porous, but pure calcium is almost impassive towards nitrogen. Metals more strongly positive than calcium accelerate the adsorption (K, Ba) ; of the others, some have no effect (Mg, Pb, Sn), others retard it (As, Sb), and some inhibit it (Bi, Cu, Zn). The addition of more positive metals has a loosening effect on the valency electrons of calcium. Calcium nitride acts as a catalytic agent in all cases. With calcium alloys containing 5 per cent. of the nitride, pure argon can be obtained from atmospheric nitrogen in a few minutes even at a temp. below 320°. H. Erdmann made this nitride by mixing calcium shavings with liquid nitrogen. L. Maquenne, and J. Ferée obtained calcium nitride by heating calcium amalgam in a current of nitrogen. The amalgam was made by the electrolysis of conc. aq. soln. of the alkaline earth chlorides with a mercury cathode. The amalgam, in an iron or nickel boat, was heated to dull redness so as to drive off the mercury, and the temp. then raised to bright redness for a short time, and the nitride allowed to cool in the gas. Platinum is attacked by the metal. In any case the product is contaminated with free metal, and some of the material from the boat. H. Herzer gave 1250° for the temp. of decomposition. L. Maquenne made **strontium nitride,** Sr_3N_2, and also **barium nitride**, Ba_3N_2, by the method used for calcium nitride. He also obtained the nitride by heating in an atm. of nitrogen, calcium, strontium, or barium oxide or other salt with magnesium or another metal capable of reducing the oxide or salt employed. The product is contaminated with magnesia. C. Limb heated a mixture of barium fluoride and sodium in an atm. of nitrogen, and obtained barium nitride. D. Wolk made barium nitride by the action of nitrogen on heated barium amalgam. H. R. Ellis made the impure nitrides of the alkaline earths by igniting a mixture of the oxide and magnesium powder in air. G. Tammann said that the reaction occurs at 700°. H. Gautier prepared the nitrides of the alkaline earths by heating an alloy of cadmium and barium, strontium, or calcium in an atm. of nitrogen. The reaction begins at 600°. A. C. Vournasos found that barium cyanamide reacts with ammonium nitrate giving barium nitride; calcium carbide, with ammonium nitrate, or calcium with mercuric cyanide, giving calcium nitride: $3Ca(CN)_2+12NH_4NO_3=Ca_3N_2+6CO_2+14N_2+24H_2O$; and $3Ca+Hg(CN)_2=Ca_3N_2+Hg+2C$. A. Guntz and R. C. Mentrel prepared barium nitride by heating barium amide in vacuo above 400° ; the reaction is reversible : $3Ba(NH_2)_2 \rightleftharpoons 4NH_3+Ba_3N_2$—the amide is formed by heating barium in ammonia gas at 300°–380°. H. Hardtung said the reaction is not perceptible after half an hour's heating at 500°, but at 575°, 0·3 per cent. of nitrogen was absorbed from ammonia. A. Guntz found that barium hydride reacts with nitrogen at a red-heat, forming barium nitride. W. Borchers and E. Beck converted metals into nitrides by electrolyzing soln. of an oxide or a salt of the nitride-forming metal in a fused mixture of alkali or alkaline earth salt, using a cathode of molten metal which does not form a nitride readily, but readily alloys with the nitride-forming metal which is liberated at the cathode. The liquid alloy is treated with a current of nitrogen when the nitride is formed. The product is treated with water or steam when ammonia is evolved, and the oxide or hydroxide of the nitride-forming metal is returned to the electrolytic chamber. The process was tried with calcium, magnesium, and aluminium. When radium is exposed to moist air, E. Ebler said that some **radium nitride** is formed even more readily than in the corresponding case with barium.

H. Moissan found that under the microscope, calcium nitride appears in the form of transparent yellowish-brown crystals; and, according to L. Maquenne, barium nitride furnishes a bronze-brown crystalline mass, or else occurs in the form of yellow needles. H. Moissan gave 2·63 for the sp. gr. of calcium nitride at 17°; and *c.* 1200° for the m.p. F. Haber and G. van Oordt said that this compound melts and vaporizes at 900°. A. Guntz and R. C. Mentrel found that barium nitride does not melt at 1000°, but at that temp. it begins to volatilize. When ammonia is heated with barium nitride at higher temp., the gas is decomposed. H. Hardtung gave 700° for the temp. of formation of calcium nitride, and 1060° for the temp. of dissociation. C. A. Kraus and C. B. Hurd found the dissociation press. of calcium nitride to be of the order $0{\cdot}3\times10^{-4}$ to $5{\cdot}5\times10^{-4}$ cm. over the range 958° to 1049°, in agreement with 113·23 Cals. for the heat of formation. A. Guntz and H. Bassett gave for the heat of formation: $3Ca_{solid}+N_{2gas}=Ca_3N_{2solid}+112{\cdot}2$ Cals.; and A. Guntz: $3Ba_{solid}+N_{2gas}=Ba_3N_{2solid}+149{\cdot}4$ Cals. A. Guntz and F. Benoit gave for the heat of formation of calcium nitride, 37·1 Cals.; for strontium nitride, 31·8 Cals.; and for barium nitride, 31·3 Cals. E. Tiede and A. Schleede found that calcium and barium nitrides are rendered luminescent by active nitrogen. I. I. Shukoff found that the sp. electrical resistance of powdered calcium nitride exceeds 2×10^6 ohms. H. Moissan, H. Gautier, K. Kaiser, and F. Haber and G. van Oordt found that when calcium nitride is heated to about 600° in a stream of *hydrogen*, ammonia and calcium hydride are formed by a reversible reaction. On the other hand, H. Erdmann and H. van der Smissen found that calcium nitride gives no perceptible ammonia when heated in hydrogen between 500° and 800°; F. Haber and G. van Oordt studied the production of ammonia by passing hydrogen over calcium nitride at 600°; and H. Hardtung obtained only about one per cent. of ammonia by allowing hydrogen to act on calcium nitride between 350° and 760° for about an hour. C. A. Kraus and C. B. Hurd found that in the system consisting of calcium, calcium hydride, and calcium nitride, an equilibrium was established near 1000° and only hydrogen was present in the gas phase. The hydrogen was ultimately all absorbed at 870°. For addition compounds with hydrogen, *vide infra*, calcium amide. According to H. Moissan, when calcium nitride is heated in *air*, it oxidizes with incandescence; and in *oxygen* oxidation begins below red-heat, and then continues without a further application of heat. L. Maquenne found that *water* decomposes these nitrides with the evolution of ammonia, *e.g.* $Ba_3N_2+6H_2O=2NH_3+3Ba(OH)_2$; alcohol has no action, but H. Moissan found that calcium nitride and absolute *alcohol*, when heated in a sealed tube, furnish ammonia; and calcium ethoxide and *ethyl chloride* at dull redness slowly form calcium chloride and carbide, and methane. Calcium nitride is decomposed by *chlorine* in the cold, and the mass becomes incandescent; similarly also with *bromine* vap.; while *iodine* acts vigorously at dull red-heat. C. Montemartini and L. Losana found that *hydrogen chloride* passed over heated calcium nitride forms calcium chloride and ammonia. Conc. *acids* decompose calcium nitride slowly, or not at all, while dil. acids act vigorously, forming calcium and ammonium salts—no gas is evolved if the nitride is pure. *Sulphur* reacts with calcium nitride at 500°, forming calcium sulphide. Contrary to R. C. Mentrel, C. A. Kraus and C. B. Hurd observed no indication of the absorption of *ammonia* by calcium and barium nitrides. According to C. Montemartini and L. Losana, *nitrogen peroxide* oxidizes the nitride slowly at a red-heat, and at a higher temp., the reaction is very vigorous, and nitrogen is evolved. Calcium nitride and *phosphorus*, at a red-heat, form calcium phosphide. At 600°, *carbon* has no action on calcium nitride, but in an electric furnace, calcium carbide is formed; at 1200°, in an atm. of nitrogen, calcium cyanide is formed. L. Maquenne observed a similar reaction with barium nitride, resulting in the formation of barium cyanide; and a similar product is obtained by the action of *carbon monoxide:* $Ba_3N_2+2CO=Ba(CN)_2+2BaO$—*vide infra,* magnesium nitride. The reaction is interesting, since it furnishes a method of fixing nitrogen as cyanide by heating a mixture of barium oxide and carbon in nitrogen. H. Hardtung found no cyanogen in the exit gases when carbon dioxide or monoxide acts on calcium nitride between 760° and 1000°, but a trace of cyanide was found in the residue. According to H. Moissan, *silicon* and *boron* have no action on calcium nitride at 100°; and *sodium, potassium,* and *magnesium* have no action at a red-heat. According to O. Schmidt, *sodium carbonate,* carbon, and calcium nitride form sodium cyanide at a red-heat: $Ca_3N_2+Na_2CO_3+C=2NaCN+3CaO$, a reaction which continues without the further application of heat.

According to A. C. Vournasos,[7] beryllium does not react with nitrogen or ammonia at an elevated temp., but **beryllium nitride,** Be_3N_2, can be made by heating beryllium in cyanogen at 800°. He also found that beryllium reacts quantitatively with the cyanides to form the nitride: $3Be+Hg(CN)_2=Be_3N_2+Hg+2C$. F. Fichter and E. Brunner observed that beryllium absorbs nitrogen from 900° upwards, but only a surface layer is formed, so that it is necessary to powder the product and repeat the process many times, in the course of which much oxide is formed. A better result is obtained by using ammonia. In both cases, the product has the formula Be_3N_2. Beryllium nitride is amorphous, but may be fused if heated rapidly to 2200° in nitrogen under atm. press., and then solidifies to colourless crystals, which scratch glass. It dissociates at 2400°. The chemical properties are similar to those of aluminium nitride. The compound is stable in air, and is only slowly decomposed by boiling water. Dil. acids and hot conc. soln. of alkali hydroxides decompose it more readily than aluminium nitride. The nitride is usually decomposed more readily than aluminium nitride. The nitride usually contains a little carbon, formed by the reaction $3Be_2C+2N_2=2Be_3N_2+3C$. Direct experiment shows that beryllium carbide absorbs nitrogen at 1250°, or reacts with ammonia at 950°–1000°, liberating carbon. A mixture of beryllia and carbon yields the nitride at 1900° in nitrogen. Cyanamide compounds are not formed.

In 1857, H. St. C. Deville and H. Caron noticed that when magnesium is distilled in air, the product is sometimes covered with small, colourless, acicular crystals which were quickly destroyed by moisture, forming magnesia and ammonia. These crystals were very probably those of **magnesium nitride,** Mg_3N_2. F. Briegleb and A. Geuther made this compound by heating magnesium in a current of ammonia or nitrogen; *e.g.* magnesium filings, in a porcelain boat, were heated to bright redness in a current of dry, acid-free nitrogen quite free from air. Some silicon is present as impurity being reduced from the silicates of the porcelain-boat; but, by using an old boat, they obtained a product almost free from that impurity. H. Hardtung found that the reaction begins at about 450°, and proceeds rapidly at 600°. A. Rossel, and G. Tammann made some observations on this subject. E. Biesalsky and H. van Eck studied the affinity of magnesium for nitrogen; and C. Montemartini and L. Losana, the partition of nitrogen and oxygen, dry or moist, between magnesium. V. Merz found the use of a very high temp. to be neither necessary nor desirable. Combination readily occurs in a glass tube heated by a gas burner. The glass is blackened during the operation owing to the liberation of silicon. A. Geuther obtained the nitride mixed with silicon by heating magnesium silicide in a current of nitrogen; and K. Kaiser, by the action of nitrogen on the heated sulphide, or the molten chloride. A. Smits, and S. Paschowetsky said that a current of ammonia acts better than one of nitrogen. A. Smits obtained the nitride by burning magnesium powder in a crucible while stirring with an iron rod; J. W. Mallet, by heating magnesium in a crucible with insufficient air for combustion to the oxide; and W. Kirchner, by burning a cylinder of magnesium, heated by a bunsen burner, in air. According to W. Eidmann and L. Möser, magnesium nitride can be prepared by heating in air magnesium powder mixed with a number of oxides of metals which readily oxidize and also by heating with certain metals and carbides. A mixture of equal parts of iron and magnesium, heated in an uncovered crucible, gave a crude product containing 36 per cent. of the nitride. By heating magnesium powder strongly in a covered crucible with a minute opening in the cover, a lower layer of nitride is formed, covered with unchanged magnesium, and a surface layer of oxide. By carefully regulating the conditions, as much as 78–80 per cent. of nitride can be obtained in the product, a value approaching very nearly to that required for a complete absorption of the oxygen and nitrogen of the air (calc. 82·3 per cent.). E. C. Szarvasy obtained the nitride by heating a mixture of graphite in an atm. of hydrogen, and then stirring the hot mixture in air ; H. Mehner, and W. Neuberger, by heating in an electric furnace a mixture of magnesia and carbon in an atm. of nitrogen ; and K. Kaiser, by passing nitrogen over magnesium hydride: $3MgH_2+2N_2=Mg_3N_2+2NH_3$; and reconverting the nitride into hydride: $2Mg_3N_2+9H_2=6MgH_2+4NH_3$. This gives a cyclic process for the fixation of nitrogen. W. Borchers and E. Beck also observed a cyclic process in which a magnesium alloy was obtained from magnesia, etc.—*vide supra*, alkaline earths. H. Hardtung heated magnesium for two hours in an atm. of ammonia, and found at different temp. the amounts absorbed to be those indicated in Fig. 12. He gave 600° for the temp. of formation, and 900° for the temp. of dissociation. H. Herzer gave 1150° for the decomposition temp.; and 1·829 to 1·872 for the sp. gr. at 25°/4°. This makes the mol. vol. between 53·9 and 56·2. W. Eidmann observed the formation of magnesium nitride when a mixture of magnesium and nitrogenous substances is heated to redness, and when magnesium is heated with boron and silicon nitrides, or the cyanides of the alkali metals, the alkaline earth metals, copper, zinc, cadmium, lead, nickel, and cobalt. A. C. Vournasos also found that magnesium reacts violently with the thiocyanates, and more quietly with the cyanides, forming the nitride : $2KCN+3Mg=Mg_3N_2+2K+2C$.

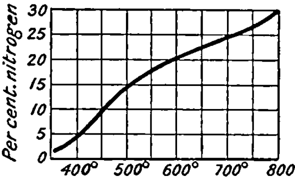


FIG. 12.—The Absorption of Nitrogen by Magnesium.

A. Remelé observed the photoelectric effect with magnesium nitride; and R. W. Riding and E. C. C. Baly studied the action of cathode rays on magnesium nitride. I. I. Shukoff found that the electrical resistance of powdered magnesium nitride exceeds 2×10^6 ohms. Magnesium nitride is a greenish-yellow, amorphous mass, which when heated, becomes yellowish-brown. N. Whitehouse found that it is not reduced by dry *hydrogen* free from oxygen, but with water-gas, magnesia, carbon, cyanamide, and other products are formed. K. Kaiser, however, represented the reaction : $Mg_3N_2+6H_2=3MgH_2+2NH_3$, and H. Hardtung obtained about 3 per cent. of ammonia by this reaction at temp. between 20° and 760° during an hour's run. F. W. Dafert and R. Miklauz observed no tendency of magnesium nitride to form addition products analogous to those with calcium and lithium nitrides. F. Briegleb and A. Geuther found that magnesium nitride is oxidized slowly to magnesia, when heated in *air;* and in dry *oxygen*, it burns with incandescence. Moist air decomposes it, and the exposed product smells of ammonia. The action of *water* is vigorous, resulting in the formation of ammonia and magnesium hydroxide. J. Lipsky studied the fixation of nitrogen by converting it into ammonia *viâ* magnesium nitride as intermediary. E. A. Schneider said that *chlorine* readily reacts with the nitride, forming magnesium and ammonium chlorides. C. Montemartini and L. Losana found that *hydrogen chloride* when heated with magnesium nitride forms the chloride and ammonia. F. Briegleb and A. Geuther found that the nitride readily reacts with conc. or dil. *hydrochloric acid*, forming magnesium and ammonium chlorides ; *hydrogen sulphide* furnishes magnesium and ammonium sulphides ; and, according to S. Paschkowetsky, the nitride is scarcely attacked by conc. *sulphuric acid* in the cold, but when heated, sulphur dioxide is evolved. F. Briegleb and A. Geuther found conc. and dil. *nitric acid* furnish magnesium and ammonium nitrates; *phosphorous chloride* gives phosphorus nitride, and, added E. A. Schneider, the reaction is vigorous at a red-heat—phosphorus distils off, the mass becomes white-hot, and the residue contains magnesium chloride and phosphorus—not magnesium phosphide. F. Briegleb and A. Geuther said that *phosphoryl chloride* can be distilled from the nitride without change, but at 170° in a sealed tube, it forms a dark-coloured mass with metaphosphoric acid in the aq. soln. Magnesium nitride is decomposed when heated to bright redness in an atm. of *carbon monoxide:* $Mg_3N_2+3CO=3MgO+2CN+C$; and likewise also with *carbon dioxide:* $2Mg_3N_2+3CO_2=6MgO+2CN+C+N_2$. These reactions have been questioned by F. Fichter and C. Schölly, who, working at 1250°, observed no formation of cyanogen, and represented the reactions: $Mg_3N_2+3CO=3MgO+N_2+3C$; and $Mg_3N_2+3CO_2=3MgO+3CO+N_2$. H. Hardtung obtained traces of cyanogen in the gas with both carbon monoxide and dioxide between 760° and 1000°; but no cyanides were found in the residue. Carbon monoxide did not react appreciably at 750°, and even at higher temp. is less reactive than the dioxide. F. Briegleb and A. Geuther observed no reaction between magnesium nitride and *alcohol* or *ethyl iodide* at 160°; A. Smits observed no change with absolute alcohol at 140°–160°; nor did an alcoholic soln. of *glycerol* or *oxalic acid* have any action, but a soln. of *urea* did change the nitride. S. Paschkowetzky found the nitride has very little action on *phenol, triphenyl phosphate, benzoyl chloride,* and *benzoic anhydride.* O. Schmidt found that *alkali carbonates* react with magnesium nitride as they do with other nitrides. A. Smits reported that magnesium nitride with *nickel chloride* yields a black substance which forms with acids a green soln. which contains some ammonia; *cobalt chloride,* and *ferric and ferrous chlorides* behave similarly, but the acid soln. has no ammonia; *silver, mercury,* and *chromium chlorides* form nitrides which are decomposed by water giving off ammonia; *platinic chloride* gives metallic platinum; and *cupric oxide or sulphate* gives copper and its nitride. There is a vigorous reaction with *lead dioxide,* and *ferrous or ferric oxide.*

K. Iwase[8] found that nitrogen is not dissolved by zinc. W. R. Grove reported what was possibly impure **zinc nitride,** Zn_3N_2, to be formed by the electrolysis of water with ammonium chloride in suspension by an anode of zinc and a cathode of platinum wire. The spongy mass collecting about the zinc rod was washed and dried. Its sp. gr. was 4·6, and it conducted electricity. When ignited, nitrogen and some hydrogen were evolved. H. N. Warren also claimed to have made zinc nitride by the electrolysis of soln. of zinc salts in presence of ammonium salts. H. Pauli could not make a nitride with a current density of 1·5–29·12 amp. per sq. m. E. Frankland said that zinc amide at a dull red-heat forms a mixture of zinc and zinc nitride. According to P. Herrmann, when zinc-dust is heated in ammonia, two compounds are formed: (i) At 500°, a grey *zinc mononitride,* ZnN, appears. It is decomposed by water slowly at ordinary temp., and rapidly when heated, forming ammonia and zinc hydroxide. With acids the mononitride develops nitrogen, and traces of hydrogen and ammonia. (ii) At 400°, a brown substance is produced in small quantities. It does not decompose boiling water, and it contains less nitrogen than the mononitride. It reacts similarly with acids. G. F. Hüttig, H. Herzer, and A. H. White and L. Kirschbraun prepared zinc nitride by passing ammonia over zinc powder at 600°. The black nitride so obtained decomposed slowly into its elements at the temp. used for its formation so that the product was always contaminated with zinc. The composition indeed depended on its speed of formation. They regarded their product as a solid soln., $Zn_3N_2.nZn$. G. G. Henderson and co-workers confirmed these results. H. Hardtung heated zinc-dust in ammonia gas at different temp. for half an hour, and found the zone of stability to be rather narrow as indicated by the curve, Fig. 13.

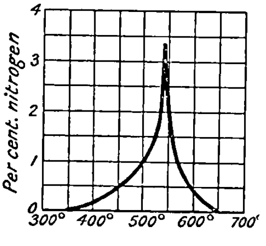


FIG. 13.—The Formation of Zinc Nitride from Zinc and Ammonia.

E. Frankland obtained zinc nitride by heating the amide to 200°, thus $3Zn(NH_2)_2=Zn_3N_2+4NH_3$; A. C. Vournasos, by heating zinc cyanide with ammonium nitrate: $3Zn(CN)_2+12NH_4NO_3=Zn_3N_2+6CO_2+14N_2+24H_2O$; and W. J. Bently and P. L. Stern, by passing ammonia—freed from oxygen and moisture—over zinc-dust—previously washed with a soln. of ammonia and ammonium chloride, alcohol, and ether, and dried in vacuo—for 30 minutes at 650°, and the product cooled below 200° before exposing it to air. The highest yield was 36·8 per cent. nitride. O. Ravner observed the formation of zinc nitride during the distillation of zinc. L. Arons made the nitride by the action of an arc between zinc poles in an atm. of nitrogen; and F. Fischer and F. Schröter, by the arc process illustrated by Fig. 11. A. Rossel found that the nitride is formed by heating a mixture of calcium carbide and powdered zinc at a red-heat. Zinc nitride prepared by the amide process is a green powder, that prepared by other processes is black. E. Frankland said that zinc nitride is decomposed by water, forming ammonia and zinc hydroxide; and with dil. acids, ammonium and zinc salts are formed. W. R. Grove prepared what seemed to be **cadmium nitride,** Cd_3N_2, by the same process as that employed for zinc nitride. It was also prepared by F. Fischer and co-workers by the method of Fig. 14; and G. S. Bohart obtained it as an orange-coloured powder by heating cadmium amide in vacuo at 180°. The black powder exploded when heated. With acids, cadmium and ammonium salts are formed. G. G. Henderson and J. C. Galletly found that cadmium behaved like zinc when heated in ammonia. P. Herrmann found that when cadmium is heated in ammonia, at about 750°, a yellow oil distils over; at 1000°, cadmium oxide is reduced by ammonia to the metal. Cadmium does not absorb nitrogen at 1000°.

J. J. Thomson and R. Threlfall[9] noticed that when an electric discharge is passed through nitrogen gas confined over mercury, there is a diminution in pressure; this was at one time attributed to the formation of a polymerization of the mol.—possibly to N_3. The phenomenon was afterwards found to arise from the union of nitrogen with mercury, probably forming mercury nitride—*vide infra.* P. Plantamour passed dry ammonia over dry but freshly prepared, yellow mercuric oxide, first in the cold, and later at 150°, and obtained an explosive substance thought to be impure **mercuric nitride,** Hg_3N_2. The product always contains some globules of mercury—even though it has been heated above 120°; the mercury may be removed by cold dil. nitric acid, and the nitride then washed and dried. If ammonia is passed over mercuric oxide—previously heated to 100°–200°—a dark grey mixture of mercury, mercurous oxide, and a small quantity of mercury nitride are formed, which, when treated with dil. nitric acid furnishes, besides mercury, cinnamon-brown curdy flakes of what was thought to be a compound of mercury nitride and nitrate. C. H. Hirzel said that mercuric oxide dried at 160° is not attacked by ammonia at 150°. H. N. Warren worked at 200°, and C. H. Hirzel repeated P. Plantamour's work, but exposed the mercuric oxide at 40°–50° to the action of the ammonia, and afterwards not over 100°; he obtained a product corresponding with mercuric nitride. T. Weyl, and H. Gaudechon said that C. H. Hirzel's product always contains oxygen, and is really dimercuriammonium oxide, $(NHg_2)_2O$—*q.v.* This substance at 125°, in contact with ammonia, forms mercuric nitride: $3(NHg_2)_2O+2NH_3=4Hg_3N_2+3H_2O$, which is associated with small globules of mercury and is like P. Plantamour's product. There is therefore some doubt as to whether the product obtained by the action of ammonia on mercuric oxide contains unchanged mercuric oxide or is a definite oxygenated compound. K. A. Hofmann and E. C. Marburg, and H. Gaudechon believe that mercuric nitride cannot be obtained by this mode of preparation. E. C. Franklin reported mercuric nitride of a high degree of purity to be formed on adding a soln. of mercuric iodide or bromide to an excess of a soln. of potassium amide in liquid ammonia: $3HgI_2+6KNH_2=Hg_3N_2+6KI+4NH_3$. The chocolate-coloured precipitate becomes darker on standing and is then more easily washed with liquid ammonia. The nitride is said to be very explosive and to require handling with great care.

Mercuric nitride of undetermined composition was stated by R. Threlfall to be formed as a brown film by the action of nitrogen on mercury when the gas under diminished press. is under the influence of an electric discharge ; and R. J. Strutt found that activated nitrogen reacts with mercury, forming a nitride. F. Fischer and F. Schröter also prepared the nitride by the process indicated in connection with Fig. 11. O. Flaschner found that scarcely any hydroxylamine is reduced by the mercury cathode.

P. Plantamour said that the impure mercury nitride, which he prepared, exploded with a white flame having a bluish-purple border when heated, when struck by a hammer, or when rubbed with a glass rod on a watch-glass. In the last case, the glass was perforated with a round hole. The explosion is said to be almost as violent as that of nitrogen iodide. According to C. H. Hirzel, mercury nitride exposed to *air* forms a dirty-white, non-explosive powder which effervesces feebly with acids : *water* slowly transforms the nitride into a white powder. E. C. Franklin's preparation exploded in contact with water, owing possibly to the presence of a trace of potassium amide. Dry *carbon dioxide* does not act on the dry nitride, but it forms with the moist powder a white substance containing carbon dioxide. E. C. Franklin said that the nitride can be dissolved in dil. *acids*. C. H. Hirzel said that conc. *nitric acid* colours the compound yellow, and then white, while dil. nitric acid transforms it into a white powder—slowly when cold, rapidly when heated. P. Plantamour found that conc. nitric acid at 40° can be made to dissolve the nitride, forming a soln. of ammonium and mercuric nitrates ; *hydrochloric acid* forms a soln. of ammonium, mercuric, and mercurous chlorides ; and boiling dil. *sulphuric acid*, a soln. of ammonium and mercuric sulphates together with a little yellow basic sulphate. The substance also explodes when brought in contact with sulphuric acid, and in that case a white powder remains behind. When heated with *potassium hydroxide*, ammonia gas is evolved, and mercury sublimed ; and C. H. Hirzel said that a cold soln. of potassium hydroxide acts slowly, and a boiling soln. rapidly forms a yellow powder, and ammonia is gradually evolved. E. C. Franklin said that the nitride is soluble in liquid *ammonia*, but not if potassium amide be also present. C. H. Hirzel found that cold aq. ammonia decomposes the nitride, forming a yellow powder ; *ammonium carbonate* acts rapidly, forming a yellow and then a white powder ; an aq. boiling soln. of *ammonium chloride* slowly dissolves the nitride with the evolution of ammonia ; and a soln. of *mercuric chloride* transforms it into a reddish-brown powder. P. Plantamour found that if mercury nitride be carefully mixed with *cupric oxide* and heated, nitrogen gas is evolved, mercury is formed, but no water.

W. H. Balmain[10] first prepared **boron nitride**, BN, by the action of molten boric acid on potassium cyanide. He considered the product of the action resembled cyanogen, and was able to unite with the metals to form compounds analogous to the cyanides, and he named the radicle *ethogen*—from αἰθός, brilliant—in allusion to its appearance in the oxidization zone of a flame. Later on, W. H. Balmain recognized that he was mistaken in assuming that ethogen is like cyanogen in forming compounds with the metals. R. Warington believed that traces of boron nitride occur in the ammonium chloride found in some volcanic districts, and assumed that it was formed from boric acid. H. St. C. Deville and F. Wöhler reported that when amorphous boron is heated to a moderate temp. in air, the boron takes fire and burns completely. The product was not all boric oxide, but rather a mixture of boron oxide and nitride. The microscopic crystals occurring in the mixture were probably those of boron nitride, for, when heated with soda-lime, they gave off ammonia. They also obtained the same substance by heating a 4 : 1 mixture of boric oxide and carbon in a current of nitrogen. W. Hempel found that under these circumstances the yield is greater if the press. be increased, thus, in 15 mins. at ordinary press., 0·014 grm. of the nitride was obtained from 3 grms. of boric acid and 2 grms. of carbon ; at 25 atm. press., 0·019 grm. ; and at 66 atm. press., 0·032 grm. H. Moissan showed that amorphous boron does not unite with nitrogen at 900°, but at 1200°, boron nitride is readily formed. E. Friederich and L. Sittig, and H. Mehner obtained it by heating a mixture of boric oxide and carbon in an atm. of nitrogen. K. Kaiser made boron nitride by the action of nitrogen on the heated sulphide. H. St. C. Deville and F. Wöhler obtained the nitride by heating amorphous boron at a dull red-heat in dry ammonia—the reaction proceeds with incandescence, and hydrogen is evolved. L. Möser and W. Eidmann heated boric oxide to 800° in a current of ammonia: $B_2O_3+2NH_3=2BN+3H_2O$; the crust of nitride which forms on the surface of the grains hinders the reaction, but if the boric oxide be mixed with twice its weight of calcium phosphate, the reaction proceeds rapidly in a blast gas-furnace. The calcium phosphate is removed by washing with a little very dil. hydrochloric acid. F. Wöhler obtained the nitride by heating a mixture of ammonium chloride and borax, and, according to H. Rose, boric oxide may be used—ammonium nitrate is not suitable. L. Möser and W. Eidmann represented the reaction: $2NH_4Cl+Na_2B_4O_7=2NaCl+2NH_3+2B_2O_3+H_2O$, and, at a higher temp., the ammonia reacts with the boric oxide; $B_2O_3+2NH_3=2BN+3H_2O$. They said that it is better to heat a mixture of borax with an inert substance like calcium phosphate so as to obtain a porous mass, and heat the product in the vap. of ammonium chloride. The calcium phosphate is removed by washing with a little very dil. hydrochloric acid. F. Meyer and R. Zappner found that the above-described processes gave very poor yields, and the only satisfactory method is to heat the boron amminochloride in a quartz glass tube, at 500°–600°, and finally at 1000° in a current of hydrogen charged with the vap. of boron trichloride and ammonia, when ammonium chloride and boron nitride are formed. The yield was 80–86 per cent. H. Davy showed that amorphous boron inflames when heated in dry nitrous oxide, and H. St. C. Deville and F. Wöhler represented the reaction with nitric oxide: $5B+3NO=B_2O_3+3BN$. The reaction proceeds *mit blendender Feuererscheinung*; but if crystalline boron be employed no reaction occurs at the softening temp. of hard glass. A. C. Vournasos showed that when boron is heated in cyanogen or hydrogen cyanide, the nitride is formed, and the same product is obtained by adding finely divided boron to fused potassium cyanide.

The potassium cyanide is first melted in a porcelain crucible at 650° in the absence of air, and poured out on a marble slab. It is then remelted in a clay or porcelain crucible, and the dry, finely-powdered element added in portions, the mixture being agitated from time to time, and the heating continued for fifteen minutes after the final addition. The cooled black mass is placed in warm water, and the insoluble residue of nitride and amorphous carbon is carefully and gently ignited in air to remove the carbon.

Boron, as an impalpable powder, reacts with many organic substances containing nitrogen—*e.g.* thiocarbamide, potassium or ammonium thiocyanate, etc.—*vide infra*, aluminium nitride. F. Wöhler obtained boron nitride by calcining a mixture of borax and anhydrous potassium ferrocyanide; W. H. Balmain used a mixture of boric acid and potassium cyanide, mercuric cyanide, cyanogen sulphide, or mellone; and M. Darmstadt, a mixture of boric oxide and urea. N. Whitehouse obtained it by heating boric oxide with carbon or carbon and iron in the presence of nitrogen; boric oxide does not form the nitride when heated in an atm. of hydrogen and nitrogen gases. C. A. Martius prepared the nitride by calcining boron amminotrichloride; A. Stock and W. Holle, from boron amminobromide; G. Gustavson, a mixture of ethylamine and boron trichloride at 200°; and A. Stock and M. Blix, boron imide, or boron imidochlorohydrate at 130°. S. Peacock obtained boron nitride by heating the oxide in an atm. of nitrogen and adding sodium when the temp. necessary for reaction is attained.

Boron nitride is a voluminous white powder which under the microscope shows no sign of crystallization. The sp. gr. depends on the temp. to which it has been ignited. F. M. Jäger and H. G. K. Westenbrink said that the X-radiogram shows that the space-lattice is either cubic with $a=7{\cdot}44$ A., or tetragonal with $a=4{\cdot}295$ A., and $c=5{\cdot}176$ A., or $a:c=1:1{\cdot}2052$. In the first case, the elementary cell contains 20 molecules, which is improbable; and in the second case, 4 or 5 molecules. The crystals were also examined by G. Hassel, who found them to be hexagonal and nearly the same as those of graphite. W. Hume-Rothery discussed the electronic structure. E. Friederich and L. Sittig said that the crystals are not cubic; the sp. gr. is 2·34; H. Herzer gave 2·321 at 25°/4°. V. M. Goldschmidt gave 2·255; and he found that the optically trigonal or hexagonal crystals have the index of refraction 1·74; and birefringence 0·3. The optical character is negative. The basal cleavage is good. The hardness is 1 to 2. The nitride melts at 3000° under press., and sublimes before melting; the electrical resistance at ordinary temp. and at the m.p. is very large. The great infusibility of boron nitride, said J. Boeseken, indicates a high degree of polymerization. L. Möser and W. Eidmann said that if the nitride be prepared at a very low temp., it appears like a colourless gelatine which dries to a hard, brittle mass which enters into reactions more readily than other forms. Thus, A. Stock and M. Blix consider that there are two forms—one much more sensitive than the other to chemical reactions; that prepared from the imide or imidochlorohydrate at 130° is an example, and if this be heated in a crucible by a blast gas-flame, it becomes insensitive to chemical action. F. Meyer and R. Zappner said the stability towards water depends on the temp. to which the nitride has been ignited. F. Wöhler said that it is stable at a high temp., and W. H. Balmain added that it is infusible. A. Magnus and H. Danz gave $2{\cdot}5153+0{\cdot}0063096(\theta-22)-0{\cdot}0_{5}32885(\theta-22)^{2}$ to represent the mol. ht. of boron nitride between 400° and 900°. R. E. Slade and G. I. Higson found that the dissociation press. of the nitride, at 1222°, is 9·4 mm.; and the heat of formation, about 69 Cals. W. Jevons attributed the bands in the spectrum of boron chloride with a little nitrogen to boron nitride; R. S. Mulliken, to boron oxide. W. Jevons also found the boron nitride bands in the arc spectrum of boron in air. W. H. Balmain discovered that boron nitride glows with a green light when held in the edge of a flame; F. Wöhler ascribed the phenomenon to the slow oxidation of the nitride. E. Tiede and F. Büscher said that only when free boric oxide is present is the nitride luminescent in the flame. The luminescence is not due to oxidation but is physical in its origin. The cause of the activation is unknown. E. Tiede and H. Tomaschek said that boron nitride exhibits luminescence only when small quantities of carbon are present. E. Tiede and A. Schleede observed that the nitride, when in contact with active nitrogen, and sensitized by flame, is phosphorescent. F. Wöhler said that boron nitride suffers no change when heated to redness in *hydrogen;* and that it does not ignite or burn when heated in *air;* but in *oxygen,* if at a high enough temp., it burns with a greenish-white flame and gives off the vap. of boric oxide. F. Wöhler, M. Darmstadt, W. H. Balmain, and L. Möser and W. Eidmann observed that in a flame the nitride phosphoresces with a greenish-white light, and oxidizes very slowly; the thermo-luminescence is hindered when much boric oxide is present. A. Remelé found that boron nitride exhibits the photoelectric effect. F. Wöhler said that *hydrofluoric acid* attacks the nitride quickly, forming ammonium fluoborate; and, added L. Möser and W. Eidmann, if the nitride be heated with *ammonium fluoride* and an excess of conc. sulphuric acid, it is completely decomposed into ammonium sulphate and boron trifluoride. According to F. Wöhler, and M. Darmstadt, *chlorine* at a moderate heat has no action, but if heated more strongly boron trichloride is formed. N. Whitehouse showed that dry *hydrogen chloride* at 1470° does not attack boron nitride; but C. Montemartini and L. Losana found that all the nitrogen is thus converted to ammonia, and boron chloride is formed. M. Darmstadt said that *hydrochloric acid* heated in a sealed tube with boron nitride at 160°–200°, forms boric acid and ammonium chloride quantitatively; but he found that *iodine* at a red-heat does not attack the nitride. L. Möser and W. Eidmann said that *sulphur dioxide* is partly reduced to sulphur by boron nitride, and F. Wöhler showed that hot conc. *sulphuric acid* slowly forms ammonium sulphate. A. Stock and M. Blix showed that the nitride formed at low temp. is rapidly dissolved by aq. *ammonia,* but not the nitride which has been calcined. F. Wöhler said that the nitride is not changed at a red-heat in an atm. of *carbon dioxide*, but L. Möser and W. Eidmann showed that the carbon dioxide is partly reduced to carbon monoxide—the boric oxide simultaneously formed as a film protects the nitride from further action. The vap. of *carbon disulphide* does not alter the nitride at a red-heat. M. Wunder and B. Jeanneret found that boron nitride is opened up when the powder is heated with *phosphoric acid* of sp. gr. 1·75. F. Wöhler showed that boron nitride acts as a reducing agent, in that molten *chromic anhydride* is reduced to chromic oxide; *molybdic anhydride*, to blue oxide; *arsenic trioxide*, to arsenic; *antimony trioxide*, to antimony; *lead*, *copper*, and *mercuric oxides*, to the metals with the formation of nitric oxide or nitrogen peroxide; and *bismuth and cadmium oxides* form a borate and nitric oxide and the latter yields some cadmium. *Zinc and ferric oxides* are not attacked. U. Sborgi and A. G. Nasini prepared nitric oxide (*q.v.*) by the action of boron nitride on *iron, copper, manganese, nickel, and cobalt oxides*. *Lead nitrate* forms lead borate. An aq. soln. of *potassium hydroxide*, said F. Wöhler, does not attack boron nitride, but with molten alkali there is a rapid evolution of ammonia. The nitride prepared at a low temp. was found by A. Stock and M. Blix to be rapidly attacked by hot dil. alkali-lye, but not so with the nitride which had been heated to a high temp. L. Möser and W. Eidmann found that when melted with *sodium dioxide*, boron nitride is converted to a borate and nitrate; and when the powdered nitride is added to the molten dioxide, there is an evolution of nitrogen and the formation of a borate with incandescence. A. C. Vournasos heated boron nitride with *sodium formate* and obtained amorphous boron, hydrogen, ammonia, and a boron hydride. F. Wöhler found that when heated with *potassium carbonate*, potassium borate and cyanate are formed: $BN+K_2CO_3=KBO_2+KOCN$; if the nitride be in excess, some potassium cyanide is formed. J. R. Morse patented a process for heating a mixture of boron nitride and potassium carbonate to dull redness whereby potassium cyanide was formed: $4BN+3K_2CO_3+2C=K_2B_4O_7+CO_2+4KCN$; if the mass be mixed with iron filings, alkali ferrocyanide is formed. W. H. Balmain, J. C. G. de Marignac, and H. St. C. Deville and F. Wöhler were not able to prepare compounds of boron nitride with the *metals*. A. Stähler and J. J. Elbert discussed a method of "fixing" the nitrogen of the atmosphere through the agency of the boron nitrides.

According to F. Briegleb and A. Geuther,[11] **aluminium nitride,** AlN, is formed by heating aluminium turnings in a hard glass tube in an atm. of nitrogen. F. Fichter and G. Oesterheld said that aluminium begins to absorb nitrogen at 750°. F. Fichter worked at 720°–740°, and in order to effect complete nitridation, he recommended finely powdering the product, and repeating the operation. J. Wolf said that the process works much more satisfactorily at 820°, and F. Fichter and A. Spengel added that the reaction started at 800° quickly rises in temp. to 1300°. N. Tschischewsky said the reaction starts at 400°, and is rapid at 1350°. Impurities may be removed by heating the product to redness in a current of dry hydrogen chloride. K. Iwase studied the solubility of nitrogen in aluminium; E. Biesalsky and H. van Eek, the affinity of nitrogen for aluminium; and C. Montemartini and L. Losana, the partition of dry or moist oxygen and nitrogen between aluminium. A. H. White and L. Kirschbaum prepared the nitride by heating aluminium to 700° in a current of ammonia. I. I. Shukoff said the reaction is vigorous at 780°. H. Moissan found aluminium nitride to be present in some commercial samples of aluminium; and L. Frank and A. Rossel, A. Rossel, E. Kohn-Abrest, and C. Matignon noted that it is formed during the oxidation of aluminium in air. H. R. Ellis obtained the impure nitride by igniting a mixture of alumina and magnesium powder in air. C. Zenghelis said that the nitride is formed if aluminium be burnt in oxygen and a current of nitrogen be substituted for oxygen while the metal is burning. L. Arons obtained it by heating aluminium by an electric current in an atm. of nitrogen. J. W. Mallet observed that by heating aluminium white-hot in a carbon crucible yellow flecks of aluminium nitride are formed. A better yield of nitride is obtained if the aluminium be bedded in sodium carbonate in a graphite crucible and heated for four or five hours. Part of the aluminium is oxidized to alumina; the soda of the sodium carbonate volatilizes; and embedded in the remaining crystals of graphite, etc., there are yellow crystalline particles, and a yellow crystalline crust of the nitride. F. Fichter strongly heated a mixture of aluminium bronze and charcoal in a covered crucible, and removed the lid when the mass was red-hot. A mixture of the oxide, carbide, and nitride was formed. L. Frank obtained the impure nitride by heating a mixture of aluminium powder and lime or calcium carbide in air. K. Kaiser prepared the nitride by the action of nitrogen on the heated sulphide. According to A. C. Vournasos, an impalpable powder of aluminium forms the nitride when heated with many organic nitrogenous compounds; thus, with thiocarbamide: $2Al+CS(NH_2)_2=2AlN+H_2S+H_2+C$; and with potassium or ammonium thiocyanate: $2KCNS+2Al=K_2S_2+2AlN+2C$, but there is a secondary reaction: $2K_2S_2+2AlN+2C=Al_2S_3+2KCN+K_2S$. Washing with alcohol gives a residue of carbon and aluminium. He also found that aluminium at 750° decomposes cyanogen and hydrogen cyanide, forming the nitride; and the same product is obtained by adding powdered aluminium to fused potassium cyanide—*vide supra*, boron nitride.

Aluminium nitride is manufactured commercially in O. Serpek's method of nitrogen fixation. Here, finely divided alumina or bauxite is mixed with carbon and heated in an atmosphere of nitrogen whereby aluminium nitride is formed: $Al_2O_3+3C+N_2=2AlN+3CO$. Bauxite reacts at 1550°, and alumina at rather a higher temp. owing to the favourable effect of the impurities—iron, silicon, nickel, manganese, and titanium oxides. The two first-named are the most active. O. Serpek said that the reaction is facilitated by gases with a small proportion of hydrogen chloride or sulphur dioxide, but S. A. Tucker and H. L. Read found sulphur dioxide to be harmful. The Badische Anilin- und Soda-Fabrik studied the effect of catalysts. The formation of the nitride from alumina and coal is greatly accelerated by the presence of 5–10 per cent. of oxides which can themselves form stable nitrides—*e.g.* those of silicon, titanium, zirconium, molybdenum, vanadium, beryllium, cerium, uranium, and chromium—as well as silicates, titanates, vanadates, etc. Silica is preferred on account of its cheapness. The presence of iron oxide and the other impurities in bauxite does not affect the catalytic agent, so that low-grade bauxite can be employed.

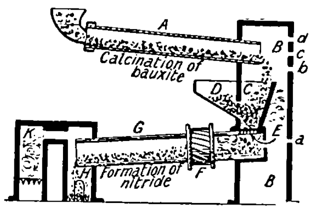


FIG. 14.—Diagrammatic Representation of O. Serpek's Aluminium Nitride Process.

The plant employed by O. Serpek consists of two superposed rotating cylindrical kilns, *A*, *G*, Fig. 14, slightly inclined towards one another and rotating in opposite directions. In the upper one, *A*, the powdered bauxite is introduced, and in its descent it is calcined and heated to about 1400° by the hot ascending gases. The calcined mass falls into the hopper, *C*, in the chamber, *B*, when it is mixed with the proper amount of coal from the hopper, *D*. The mixture enters the nitriding kiln, *G*, *viâ* openings, *E*, and then passes through a zone heated to 1800°–1900° by the detachable electric furnace, *F*, and lined with briquettes of aluminium nitride. The nitride collects in the chamber *H*. Producer gas passes from the producer *K*, enters the nitriding kiln flowing contrawise to the charge, is enriched by the carbon monoxide generated by the nitriding reaction. It leaves the kiln *G* and rising into the chamber *B* meets a current of air from *a*, *b*, *c*, *d*, it then enters the chamber *A*, and burns to carbon dioxide. O. Serpek stated that a mixture of hydrogen and nitrogen gives better results than producer gas in the rotary furnace. He also abandoned the rotary furnace in favour of a short chamber. The carbon-bauxite mixture was dropped through the nitrogen at 1250°–1300°, and the conversion is said to take place more rapidly than the 5–6 hrs. required in the rotary kiln. The aluminium nitride is then decomposed by water or alkali-lye, preferably, when ammonia is formed: $AlN+3H_2O=NH_3+Al(OH)_3$. If alkali-lye be used, the nitrogen is thus recovered as ammonia, and the alumina, virtually free from silica and iron, can be used for the production of alumina. The Badische Anilin- und Soda-Fabrik studied the best methods of treating the nitride with acid or alkali so as to recover the ammonia. The presence of soluble salts, like sodium chloride, favour the elimination by alkali-lye. W. Borchers and E. Beck tried a process involving electrolysis as indicated in connection with the alkaline earth nitrides—*vide supra.* O. Serpek's process has been discussed by T. H. Norton, E. Donath and A. Indra, J. W. Richards, O. Nissen, E. B. Maxted, C. Matignon, F. Marre, G. L. Bourgerel, W. von Escher, E. Bronnert, M. Shoeld, G. Herman, etc.

O. Serpek first used aluminium carbide as the raw material; and N. Caro showed that the absorption of nitrogen was then probably preceded by the dissociation of the carbide into carbon and aluminium. Better results were obtained commercially by heating a mixture of alumina and carbon in a current of nitrogen or producer gas; and O. Serpek here assumed that aluminium carbide is first formed, but there is no need for this assumption. S. A. Tucker and H. L. Read found that very little change takes place when the mixture of alumina and carbon is heated in nitrogen at 1600°; the reaction proceeds well at 1800°–2000°; but above 2000°, there are signs of a decomposition of the nitride. W. Fränkel showed that the velocity of absorption of dry nitrogen by a 2 : 1 mixture of alumina and carbon, is very small at 1350°; it increases to a moderate speed at 1500°, and above that temp. the absorption is rapid. Thus, in 30 mins.:

	1350°	1400°	1450°	1500°	1550°	1600°
Nitrogen absorbed .	0·2	3·1	4·4	8	19·5	24·5 per cent.

S. Peacock and E. I. du Pont found that a 3 : 1 mixture reacts with nitrogen at 1500° below 500 mm. press., forming *aluminium carbonitride*, $Al_2C_3N_6$, thus: $Al_2O_3+6C+3N_2=Al_2C_3N_6+3CO$; but W. Fränkel observed no indications of the formation of such a compound, at press. down to 250 mm. By working in atm. with variable proportions of nitrogen and carbon monoxide, he was able to show that the reaction: $Al_2O_3+3C+N_2\rightleftharpoons 2AlN+3CO$, is reversible. At one atm. press., and 1500°, the equilibrium conc. of carbon monoxide is between 25 and 40 per cent.; and at 1600°, between 50 and 65 per cent. At 1700°, nitrogen was still absorbed from an atm. with 70 per cent. carbon monoxide. Hence, by working with producer gas, a higher temp. is required than when working with an atm. of nitrogen. W. Hoopes, and N. F. O. Palacin made an impure nitride from the nitrogen in flue-gases. According to H. J. Krase and co-workers, if a ferro-aluminium containing 50 per cent. aluminium is heated at 1400° in nitrogen under atm. press., about 60 per cent. of the aluminium is converted into nitride. The presence of small amounts of magnesium promotes nitrification, whilst calcium, silicon, and titanium have the opposite effect. If small quantities of cryolite, or of the chlorides or fluorides of aluminium, magnesium, sodium, or calcium are present, nitrification may be rapid and practically complete even at 1200°. With ferrotitanium or aluminium carbide at 1400° the absorption of nitrogen is only about 20 per cent. of the theoretical, and with ferrosilicon, 2 per cent. C. Matignon found carborundum crystals in aluminium nitride made by passing nitrogen over a heated mixture of alumina and coke—the silicon was derived from the silica in the coke.

Aluminium nitride has been reported as a pale yellow, medium yellow, and and bluish- or greyish-black powder; and that prepared by J. W. Mallet was said to have some short rhombic prisms with the end faces making an angle of 120°. H. Ott found that the X-radiogram gave no evidence of a polar structure of the crystals. The crystals are hexagonal, with $a=3{\cdot}113$ A., and $c=1{\cdot}601$. The aluminium and nitrogen atoms are separately distributed in close, spherically packed, hexagonal lattices which are slightly compressed in the direction of the six-fold axis of symmetry, and displaced in the same direction. The basal group comprises two molecules, and each atom of either kind is surrounded tetrahedrally by four atoms of the other kind arranged at a uniform distance of 1·894 A. W. Hume-Rothery, and H. G. Grimm and A. Sommerfeld discussed the electronic structure. H. Herzer gave 3·045 to 3·053 for the sp. gr. at 25°/4°; 13·4 for the mol. vol.; and >1400° for the temp. of decomposition. C. Matignon said that aluminium nitride does not melt at 2200°, and at higher temp., it dissociates into its elements. K. F. Niessen studied the ionic charges in the crystals of the nitride. E. Friederich and L. Sittig gave 2200° for the m.p. under 4 atm. press. H. Hardtung gave 1100° for the temp. of formation and 1400° for the temp. of decomposition of aluminium nitride. The formation of the nitride is a strongly endothermal reaction. J. W. Richards gave —213·22 Cals., and W. Fränkel, —243 Cals. F. Fichter and E. Jenny gave (Al,N)=61·0 Cals.; and $2AlN+3O=Al_2O_3+N_2+258{\cdot}2$ Cals.; and for the heat of oxidation: $2AlN+3O=Al_2O_3+N_2+258{\cdot}2$ Cals. R. W. Riding and E. C. C. Baly studied the action of the cathode rays on the nitride. I. I. Shukoff found that the electrical resistance of the powdered aluminium nitride exceeds 2×10^6 ohms. H. Hardtung, and F. Fichter and A. Spengel said that *hydrogen* is without action on the nitride; but, according to F. Fichter, it decomposes when heated to redness in *oxygen*, forming alumina and nitrogen; and, according to J. W. Mallet, when heated in *air*, it becomes grey owing to the separation of alumina, but even after two hours' roasting in air, it still contained nitrogen. In moist air, the nitride gradually becomes sulphur-yellow and it crumbles to powder, forming aluminium hydroxide and ammonia. It is decomposed by *water* giving off ammonia: $AlN+3H_2O=NH_3+Al(OH)_3$. The Badische Anilin- und Soda-Fabrik worked out methods for treating the crude nitride to recover the ammonia, and obtain aluminium hydroxide of a high degree of purity. Thus, the crude nitride containing say silicon nitride can be treated with limited amounts of acid or alkali so as to obtain the alumina in a soluble form free from silica. It is also possible to arrange the proportion of acid or base so that the aluminium hydroxide remains insoluble: $2AlN+H_2SO_4+6H_2O=2Al(OH)_3+(NH_4)_2SO_4$. F. Fichter and A. Spengel said that dry *halogens* act slowly on the nitride—*chlorine* decomposes it at 760°, thus: $2AlN+3Cl_2=2AlCl_3+N_2$; while dry *hydrogen chloride* at a red-heat merely volatilizes some of the impurities in the nitride; but C. Montemartini and L. Losana found the nitrogen can be thus converted to ammonia and aluminium chloride is formed. The nitrogen is partly displaced when the nitride is heated with *sulphur*, and with *carbon disulphide* vapour. The nitride is rapidly decomposed by *sulphur chloride* vapour; and by heating with a mixture of 10 c.c. of conc. *sulphuric acid* and 40 c.c. of water. When heated with *phosphorus*, the nitrogen is partially displaced, but *phosphorus trichloride* is without action. There is no reaction with *carbon* at 1200°, and *carbon dioxide* acts as an oxidizing agent. H. Hardtung observed no formation of cyanide with *carbon monoxide* or carbon dioxide. F. Fichter and A. Spengel found that when aluminium nitride is fused with a mixture of *alkali carbonates*, and carbon, a large part of the nitride is converted into cyanide. Aluminium nitride and *alcohol*, at 230°, form triethylamine. Fused *potassium hydroxide* decomposes the nitride: $AlN+3KOH=K_3AlO_3+NH_3$; and the reaction with *sodium dioxide* is incomplete —some nitrate is formed. Fused *lead dichromate* decomposes the nitride completely. N. Tschischewsky found that aluminium nitride dissolves in iron, and if aluminium is present in iron, it can retain and hold nitrogen as aluminium nitride.

F. Fischer and co-workers [12] reported **indium nitride**, InN, and **thallium nitride**, TlN, to be formed by the process outlined in connection with Fig. 11. According to E. C. Franklin, the interaction of liquid ammonia soln. of thallium nitrate and potassamide according to the equation: $3TlNO_3+3KNH_2=Tl_3N+3KNO_3+2NH_3$, yields a dense black precipitate of the **thallous nitride**, Tl_3N, which is readily soluble in excess of potassamide and also in liquid ammonia soln. of ammonium nitrate. In the latter case, the thallium nitride is reconverted into nitrate, thus: $Tl_3N+3NH_4NO_3=3TlNO_3+4NH_3$. E. Friederich and L. Sittig obtained **scandium nitride**, ScN, by heating a mixture of the oxide and carbon in nitrogen gas. E. Friederich gave *c.* 2920° for the m.p. and said that no perceptible volatilization occurs at the m.p. He gave 3·08 ohms for the sp. electrical resistance. K. Becker and F. Ebert found that scandium nitride has cubic crystals with an X-radiogram corresponding with a density 4·21, and an elementary cube of side 4·44 A. L. Pauling discussed the lattice-structure. E. Friederich and L. Sittig gave 4·2 for the sp. gr., and 2650° for the m.p. There is no perceptible volatilization at the m.p. C. Matignon prepared **lanthanum nitride,** LaN; **praseodymium nitride,** PrN; **neodymium nitride,** NdN; and **samarium nitride,** SaN, by heating a mixture of the oxide with powdered magnesium or aluminium in an atm. of nitrogen; or heating the chloride with sodium in an atm. of nitrogen. W. Muthmann and K. Kraft found that lanthanum does not burn in nitrogen, but the metal absorbs the gas at a red-heat, 850°–900°. When lanthanum is burnt in dry air, more than half is converted into nitride; the union of lanthanum with nitrogen commences at a lower temp. than is the case with oxygen (440°–460°). It is also formed when lanthanum is heated in dry ammonia. A. C. Vournasos made lanthanum nitride by heating the metal in cyanogen or hydrogen cyanide at 750°, or by adding the finely divided metal to fused potassium cyanide as in the case of boron nitride—*vide supra.* Lanthanum nitride is stated by W. Muthmann and K. Kraft to be a dull black solid which slowly decomposes in moist air with the evolution of ammonia. It reacts with water less violently than cerium nitride: $LaN+3H_2O=La(OH)_3+NH_3$; and with acids it forms salts of lanthanum and ammonium. G. Tammann measured the rates of formation of lanthanum nitride. E. Friederich and L. Sittig obtained impure **ytterbium nitride,** and lanthanum nitride, by heating a mixture of the oxide and carbon in nitrogen. E. Friederich and L. Sittig made **erbium nitride,** ErN, by the action of nitrogen on a heated mixture of erbia and carbon.

The **carbon nitrides** are represented by cyanogen as a type; and these compounds are discussed elsewhere. Three **silicon nitrides** have been reported, *viz.* SiN, Si_3N_4, and Si_2N_3. H. St. C. Deville and F. Wöhler[13] employed an ingenious method for preparing silicon nitride. Crystalline silicon was placed in a crucible which was placed in a larger crucible with carbon packing in the annular space between the two crucibles. The combination was heated white-hot. The penetration of oxygen from the air to the inner crucible was prevented, while atm. nitrogen could pass the carbon into the inner crucible. The preparation of nitrogen as a separate process is not therefore necessary. G. Tammann said that no reaction occurs between nitrogen and silicon at 700°. The union of the two elements furnishes **silicon hemitrinitride,** Si_2N_3. P. Schützenberger and co-workers obtained the same white product; they removed the free silicon by washing with potashlye.

According to P. Schützenberger and A. Colson, *carbazot-silicium,* or *silicon dicarbonitride,* Si_2C_2N, is formed when crystallized silicon is heated to whiteness in a brasqued crucible. The product, after washing with boiling potash to remove silicon, and treatment with hydrofluoric acid to remove silica and silicon nitride, is a bluish-green, pulverulent mass. Silicon dicarbonitride is insoluble in alkalies and in all acids. Heated to redness in oxygen or with cupric oxide, it undergoes no sensible change, but when heated with litharge, lead dioxide, or a mixture of litharge and lead chromate, it burns brilliantly, with formation of oxides of nitrogen and carbon dioxide. L. Weiss and T. Engelhardt found that heating silicon in the flame of a coke fire gives a product approximating *silicon tricarbonitride,* Si_3C_3N. A. Colson obtained *silicon cyanide,* SiCy, by the action of mercuric cyanide on silicon disulphide in dry benzene.

According to L. Wöhler and O. Bock, when nitrogen is passed over calcium disilicide heated at 1150°, a grey mass containing about 22·5 per cent. of nitrogen is formed. This consists principally of **calcium silicocyanamide, or calcium silicodinitride,** $CaSiN_2$, **calcium silicocyanide, or calcium disilicodinitride,** $Ca(SiN)_2$, and silicon, $2CaSi_2+2N_2=CaSiN_2+Si+Ca(SiN)_2$, together with small quantities of calcium nitride, Ca_3N_2, and silicon nitride, Si_3N_4. Under similar conditions, calcium monosilicide yields first an intermediate product, **calcium siliconitride,** CaSiN, or $Ca_2Si_2N_2$, $Ca_2Si_2+N_2=Ca_2Si_2N_2$; and then calcium silicocyanamide, $Ca_2Si_2N_2+N_2=2CaSiN_2$, but a considerable portion of the monosilicide is transformed into disilicide and calcium during the heating. Neither calcium silicocyanamide nor calcium siliconitride could be isolated from the reaction products, but both substances dissolved in hydrochloric acid without separation of silica. The rate of absorption of nitrogen by calcium disilicide is greatly accelerated by addition of calcium chloride or of less than 5 per cent. of calcium fluoride to the reaction mixture and takes place at temp. as low as 850° in the presence of these catalysts. In the presence of 50 per cent. of calcium chloride, a mixture of lime and ferro-silicon containing 90 per cent. Si absorbs 20·7 per cent. of nitrogen at 1050°–1100°, forming calcium silicocyanamide and calcium metasilicate. Barium oxide and magnesia under similar conditions give analogous products. Calcium silicocyanide is insoluble in hydrochloric acid, but soluble in a mixture of hydrofluoric and sulphuric acids, to which it yields its nitrogen as ammonium salt.

A. Geuther said that the reaction between silicon and nitrogen occurs only slowly below the m.p. of silicon; and at a bright red-heat, calcium or magnesium silicide in an atm. of nitrogen furnishes only the nitride of the more basic element, the silicon separates in its elemental state. E. Vigouroux observed no reaction between amorphous silicon and nitrogen at 1000°, but at a higher temp., a nitride was formed. H. Mehner obtained the nitride from a heated mixture of silica and carbon in an atm. of nitrogen. According to L. Weiss and T. Engelhardt, when silicon is heated in a porcelain boat in an atm. of nitrogen, combination begins above 1250°, since they found that after half an hour's heating at different temp., the nitrogen absorbed per gram of silicon was :

	1295°	1300°	1310°	1320°	1400°	1480°
Nitrogen . .	0·0001	0·0001	0·0002	0·0014	0·0049	0·0061 gram

N. Tschischewsky made the nitride by working at 1400°. About 4 per cent. of the silicon volatilizes during the reaction. The product obtained after heating the silicon in nitrogen for an hour is an amorphous, voluminous, white powder which, under the microscope, seems to consist of several different substances. The composition of the final product is dependent on the mode of purification; if boiled with potassium hydroxide soln., followed by treatment with hydrofluoric acid, a product containing silicon hemitrinitride mixed with silica is obtained. The silica could not be removed from the nitride. M. Blix and W. Wirbelauer obtained the nitride by heating silicam, Si_2N_3H, between 1200° and 1400°; and H. St. C. Deville and F. Wöhler, by the action of ammonia on silicon chloride.

According to P. Schützenberger, when silicon tetrachloride is sat. with dry ammonia, a white compound, *silicon decanitridohydrotrichloride*, $Si_8N_{10}Cl_3H$, is formed, and this is decomposed by water with the separation of silica; when heated in a current of ammonia, *silicam*, Si_2N_3H, is formed. Later, P. Schützenberger said that dry ammonia converts silicon tetrachloride into *silicon hexanitridodichloride*, $Si_5N_6Cl_2$, thus: $5SiCl_4+24NH_3=18NH_4Cl+Si_5N_6Cl_2$; and this when heated with ammonia forms silicam, $2Si_5N_6Cl_2+7NH_3=4NH_4Cl+5Si_2N_3H$. This subject was discussed by J. Persoz, and J. A. Besson.

According to H. St. C. Deville and F. Wöhler, and P. Schützenberger, silicon hemitrinitride is a white, amorphous substance which does not melt in ordinary furnaces. W. Jevons attributed the bands in the spectrum of silicon tetrachloride with a little air to the formation of a silicon nitride. R. S. Mulliken, E. Woldering, and W. Jevons studied the band spectrum of silicon nitride. According to H. St. C. Deville and F. Wöhler, and P. Schützenberger, silicon heminitride is not altered when heated in air; but in moist air it slowly decomposes, and smells of ammonia. The same remark applies to the action of water at ordinary temp. It is decomposed by steam, with the formation of amorphous silica. The nitride is decomposed by hydrofluoric acid, forming ammonium fluosilicate, and, according to P. Schützenberger, liberating ammonia. Dry chlorine has no action at a bright red-heat; and aq. acids and alkalies have no action on the nitride. Molten potassium hydroxide dissolves it with the liberation of ammonia, and the formation of potassium silicate; molten potassium hydroxide forms potassium cyanate, and if the nitride is in excess, potassium cyanide. When heated with red-lead, nitrogen trioxide is formed with incandescence, and when fused with lead dichromate, nitrogen gas is given off. L. Weiss and T. Engelhardt gave 3·22 for the sp. gr. of the product with 19·84 per cent. SiO_2, and 3·64 for the pure nitride. Its properties resemble those of the normal nitride.

L. Weiss and T. Engelhardt found that if the product of the action of nitrogen on silicon at 1300°–1400° be treated with a mixture of nitric and hydrofluoric acids, the hemitrinitride is probably broken down, because the residue has the composition of **silicon mononitride,** or **silicocyanogen,** SiN, plus about 13·55 per cent. SiO_2. The sp. gr. of the impure nitride is 2·99, and of the pure nitride, 3·17. It loses 36·6–44·8 per cent. of its nitrogen content by heating 3–6 hrs. with conc. sulphuric acid. Its properties resemble those of the normal nitride. P. Schützenberger claimed to have prepared this nitride in 1879.

L. Weiss and T. Engelhardt showed that if silicon be heated between 1300° and 1400° in an atm. of nitrogen, the progress of the absorption from hour to hour is as follows:

Time . . .	1st	2nd	3rd	4th	5th	6th	7th
Increase in weight	22·47	11·68	10·87	4·74	1·81	0·92	0·05 per cent.

so that the total amount of nitrogen absorbed was 58·54 per cent. This corresponds very nearly with that required for *normal silicon nitride*, or **silicon tritatetranitride,** Si_3N_4. P. Schützenberger claimed to have prepared this nitride in 1879. E. Friederich and L. Sittig made it by the action of silica, carbon, and nitrogen at 1250°–1300°. According to H. Funk, the finely divided silicon obtained by cooling a 10 per cent. soln. of that element in aluminium forms this nitride after 10 mins.' heating in nitrogen at 1450°, whereas crystalline silicon requires several hours. L. Weiss and T. Engelhardt found that this compound is a greyish-white amorphous powder, whose sp. gr. when contaminated with 9·67 per cent. of silica was 3·26, thus leaving 3·44 for the pure nitride. E. Friederich and L. Sittig gave 3·44 for the sp. gr., and said that the crystals are not cubic. They gave 1900° for the m.p. under press., and found that the nitride sublimes before melting. The electrical resistance is very large. Silicon nitride is very inert chemically. Water vapour at 100° has very little action, the merest trace of ammonia can be detected; a similar result was obtained with superheated steam at 800°. Dil. acids, excepting hydrofluoric acid, have no action; but heating with conc. sulphuric acid results in the slow production of ammonium sulphate—after 3–6 hrs.' heating, 42·1–45·8 per cent. of the contained nitrogen was given off. Hydrofluoric acid decomposes the nitride, especially after a preliminary treatment with potassium hydroxide, forming ammonium fluosilicate; but it is fairly stable in contact with a mixture of nitric and hydrofluoric acids. Ammonia is evolved when the nitride is fused with potassium hydroxide; and when heated with potash-lye, nitrogen is given off. Lead chromate, lead dioxide, and lead monoxide are reduced with the evolution of nitrogen. N. Tschischewsky found molten iron dissolves about 0·75 per cent. of silicon nitride.

The Badische Anilin- und Soda-Fabrik prepared a nitride of undetermined composition by heating a mixture of silica and carbon in an atm. of nitrogen. The reaction proceeds at a relatively low temp. if a hydroxide or salt of a metal be added. The product contains silicon nitride mixed with the nitride of the metal. The Badische Anilin- und Soda-Fabrik also removed many of the impurities—iron, carbon, silicates, carbides, silicides, and phosphides—by treatment with acids or mild oxidizing agents which do not affect the silicon nitride. A. S. Larsen and O. J. Storm prepared the nitride by the action of nitrogen on molten silicides—*e.g.* ferrosilicon.

In 1850, F. Wöhler[14] drew attention to the magnitude of the affinity of nitrogen for titanium, for the two elements readily unite together at a high temp., forming **titanium nitride**; and F. Wöhler and H. St. C. Deville said that it is difficult to prepare titanium by reduction because of the penetration of atm. nitrogen into the heated vessel and the consequent formation of the reddish-brown nitride. Four nitrides have been reported, *viz.*, TiN, Ti_5N_6, Ti_3N_4, and TiN_2. There is some doubt about the chemical individuality of the first, second, and last of these substances. F. Wöhler and H. St. C. Deville obtained the nitride by heating a mixture of sodium and potassium fluotitanate in a porcelain boat in a hard glass tube through which a current of nitrogen was passed. The salt was transformed into a bronze-coloured mass of the nitride. They also obtained titanium nitride by passing a mixture of hydrogen and nitrogen, carrying the vapour of titanium tetrachloride, over molten sodium, or aluminium; by passing nitrogen over a fused mixture of potassium fluotitanate, sodium chloroaluminate, and aluminium. H. Mehner heated a mixture of titanic oxide and carbon in an atm. of nitrogen. A. E. van Arkel and J. H. de Boer obtained the nitride by passing the vapour of the chloride mixed with nitrogen over a heated tungsten filament. G. Tammann noted a formation of a film of nitride when titanium is heated in nitrogen. F. von Bichowsky described the manufacture of this compound. The Titan Co., and F. von Bichowsky and J. Harthan obtained impure titanium nitrides for the production of ammonia by treatment with acids.

C. Friedel and J. Guérin claimed to have prepared **titanium mononitride,** or **titanocyanogen,** TiN, or Ti_2N_2, by the action of dry ammonia on titanic oxide, or titanium sesquioxide at a red-heat; by heating titanium tritatetranitride at a dull red-heat in a stream of dry hydrogen or ammonia; and by the action of cyanogen on a mixture of titanic oxide and carbon at a bright red-heat. H. Moissan obtained it by melting titanic oxide—with or without carbon—titanium, or titanium carbide in a high temp. electric furnace. E. Friederich and L. Sittig made it by the action of carbon or hydrogen on titanic oxide at 1300° followed by treatment with nitrogen. L. Weiss and H. Kaiser obtained it by heating titanium in a stream of nitrogen in a porcelain tube at 1400°; and O. Ruff and F. Eisner, by heating the tetratritanitride in a stream of ammonia at 1500°. H. Hardtung obtained the nitride by heating titanium in ammonia for 6 hrs. at 900°–1000°. G. G. Henderson and J. C. Galletly prepared a nitride by the action of ammonia on heated titanium. The Badische Anilin- und Soda-Fabrik has discussed the purification of the nitride by the process indicated in connection with silicon nitride. H. Moissan described it as a hard, tough, fusible, bronze-coloured mass which has a sp. gr. of 5·18, and is hard enough to scratch the ruby, but can be scratched by the diamond; O. Ruff and F. Eisner gave 5·10 for the sp. gr. at 18°; and C. Friedel and J. Guérin say that it is an amorphous, brass-yellow powder which has a sp. gr. of 5·28 at 18°, and is hard enough to scratch the topaz. H. Herzer gave 5·122 for the sp. gr. at 25°/4°; and 12·1 for the mol. vol. E. Friederich and L. Sittig gave 5·18 for the sp. gr.; 2927° for the m.p.; and found the space-lattice to correspond with a face-centred cube of the sodium chloride type with edge 4·40 A.; A. E. van Arkel gave 4·23 A. There are 4 mols. in each elementary cell. The compound melts at 2930° and does not sublime before melting. It is a good conductor of electricity, the sp. resistance being $1·3\times10^{-4}$ ohm at room temp., and $3·4\times10^{-4}$ ohm at the m.p. I. I. Shukoff observed that the electrical conductivity of powdered titanium nitride, 31·05 mhos, is of the same order as that of the metals, and he therefore argued that the titanium nitrides are not chemical compounds but solid soln. of nitrogen in titanium. C. Friedel and J. Guérin showed that when heated in air, it oxidizes to titanic oxide; with molten potassium hydroxide, it furnishes ammonia; it is dissolved by sulphuric acid with the evolution of sulphur dioxide; and when heated with copper oxide to redness, the nitrogen is all driven off. E. Friederich and L. Sittig found the bronze-yellow nitride is insoluble in boiling sulphuric, nitric, or hydrochloric acid, but it is quickly dissolved by hot *aqua regia;* boiling potash-lye or soda-lye furnishes ammonia. O. Ruff and F. Eisner said that neither chlorine gas at 270°, nor liquid chlorine is able to convert it into chloronitride; and C. Montemartini and L. Losana showed that when the nitride is heated in a current of hydrogen chloride, titanium chloride and ammonia are formed; and they studied the partition of dry or moist oxygen and nitrogen between titanium.

F. Wöhler said that *titanium pentitahexanitride,* Ti_5N_6, is formed when the tetratritanitride is heated in a current of hydrogen until, below redness, the evolution of ammonia begins. It is said to remain undecomposed when heated in air at about 1083°. C. Friedel and J. Guérin said that this compound is an impure form of the mononitride. F. Wöhler calcined titanic oxide in a stream of dry ammonia, cooled the product in the same gas, and obtained what he regarded as *titanium dinitride*, TiN_2. O. Ruff claimed to have made the dinitride by heating titanic oxide to at least 1000°—better at 1400°–1500°—in a current of dry ammonia. H. Geisoff did not obtain it by the action of ammonia on liquid titanium tetrafluoride. F. Wöhler and H. St. C. Deville did not obtain it by strongly heating titanic oxide in a current of mixed hydrogen and nitrogen gases. The dinitride was said to be a dark violet powder with a coppery appearance like sublimed indigo. Its properties resemble those of the hexapentitanitride. C. Friedel and J. Guérin, and P. Hermann regarded the dinitride as an impure form of the mononitride ; and O. Ruff and F. Eisner say that the nitrides Ti_2N, TiN_2, and Ti_3N_4 are impure forms of TiN.

H. Rose's first report of the isolation of titanium shows that he had mistaken what F. Wöhler called *Stickstofftitan* for elemental titanium. This substance is really **titanium tritatetranitride,** Ti_4N_3. It is also probable that the titanium reported by C. Despretz to be formed from titanium tetrachloride as a brown powder was really this nitride. H. Rose, J. Persoz, and J. von Liebig obtained it by the action of heat on titanium amminochloride ; F. Wöhler, by passing the vapours of ammonium and titanium chlorides through a red-hot tube. H. Geisoff used a mixture of the vapour of ammonia and titanium tetrachloride. E. A. Schneider found that F. Wöhler's nitride always contained up to 5·4 per cent. of oxygen. C. Friedel and J. Guérin recommended driving the air out of the apparatus with a stream of hydrogen chloride. O. Ruff and F. Eisner, and N. Whitehouse obtained this nitride by heating titanium amminochloride in a stream of ammonia. J. von Liebig described this nitride as forming a dark violet-blue powder, or coppery-looking mass resembling sublimed indigo. W. Hermann said that the violet colour produced by titanium in the blowpipe bead with fused microcosmic salt is really titanium nitride ; and suggested that titanium nitride may be the pigment in the amethyst. C. Friedel and J. Guérin said that it forms what are probably rhombohedral crystals. K. Becker and F. Ebert found the X-radiogram of the cubic crystals corresponded with a sp. gr. 4·81, and an elementary cube of side 4·40 A. H. Rose said that a thin film on glass is red in reflected and green in transmitted light. F. Versmann said that a bright yellow colour is formed when this nitride is heated in *hydrogen ;* but H. Hardtung obtained only one per cent. of ammonia during an hour's action of hydrogen on titanium nitride at 1000°. In 1872, C. M. Tessié du Motay suggested obtaining nitrogen from the atmosphere by first making the tritatetranitride, and then splitting off nitrogen and ammonia by heating the product in a current of hydrogen so as to produce the mononitride. The mononitride can be transformed into the tritatetranitride by heating it in a current of nitrogen, and thus the cycle begins anew. According to F. Wöhler, when heated in *air,* it oxidizes to titanic oxide in a crystalline form. When the oxidation is nearly ended, the product emits a noise possibly due to an allotropic change in the titanic oxide. The nitride forms titanium tetrachloride when heated in *chlorine,* and if an intimate mixture of nitride and *carbon* is heated in chlorine, it does not form $TiCl_4.CyCl$. C. Montemartini and L. Losana observed that when heated in *hydrogen chloride,* the nitrogen is quantitatively converted into ammonia. H. Hardtung observed no formation of cyanides during the action of *carbon monoxide* or of *carbon dioxide* on titanium nitride. The Badische Anilin- und Soda-Fabrik reported that if this nitride be mixed with carbon and the oxides, or salts of the alkali or alkaline earth metals, and fused, cyanides or cyanamides are produced. O. Ruff and F. Eisner said that the nitride is insoluble in dil. *acids ;* it is decomposed by hot conc. *sulphuric acid,* and conc. *nitric acid,* especially if *hydrofluoric acid* be also present. H. Rose found the nitride dissolves with difficulty in hot nitric acid, but readily in *aqua regia.* M. Wunder and B. Jeanneret found that titanium nitride is opened up by heating it with *phosphoric acid* of sp. gr. 1·75. O. Ruff and F. Eisner said that the nitride is decomposed by a boiling soln. of *potassium hydroxide.* I. I. Shukoff considers the so-called titanium nitride to be solid soln. H. B. Landmark patented a process for fixing the nitrogen of the atm. by means of titanium nitride and the subsequent conversion of the nitrogen into ammonia.

Like titanium, zirconium readily forms a nitride when heated in an atm. of nitrogen. This was demonstrated by J. W. Mallet,[15] who worked with zirconium contaminated with aluminium; by E. Wedekind, who worked with a metal contaminated with magnesium; and by C. Matignon. E. Wedekind also obtained the nitride by heating the carbide to redness in an atm. of nitrogen. J. W. Mallet heated amorphous zirconium in a lime crucible at about 1750°. Amorphous zirconium in an atm. of ammonia at a dull red-heat forms the nitride with incandescence. E. Wedekind, and F. P. Venable and R. O. Dietz found that when zirconium chloride is heated in ammonia, or amorphous zirconium in cyanogen gas, the nitride is formed. Two nitrides have been reported, Zr_2N_3, and Zr_3N_8. The former is the more clearly defined. Powdered zirconium, dried, and freed from gases, combines directly with but relatively small amounts of nitrogen when heated in that gas below 1000°; thus, at 800°, the metal took up 1·6 per cent. of gas, but when heated to 1050°, the metal acquired a yellow or olive-green colour, and finally became grey. The product contained 9·24 per cent. of nitrogen corresponding with zirconium : nitrogen=3 : 2. A. E. van Arkel and J. H. de Boer made zirconium nitride by the process they used for the titanium nitride. So also with **hafnium nitride**. F. Wöhler, and J. M. Matthews obtained **zirconium tritaoctonitride**, Zr_3N_8, by gradually raising the temp. of zirconium octamminotetrachloride in an atm. of nitrogen. The grey powder burns in air to form zirconia. P. Bruère and E. Chauvenet could not prepare either Zr_3N_8 or Zr_2N_3. By heating zirconium tetramminotetrachloride at 300°, they obtained **zirconium tritatetranitride**, Zr_3N_4, and not F. Wöhler's Zr_3N_8. E. Friederich and L. Sittig represent the pale yellowish-brown powder obtained by heating zirconium oxide and carbon in nitrogen as **zirconium nitride**, ZrN. The space-lattice is a regular face-centred cube of the sodium chloride type, with sides 4·63 A. There are four mols. per unit cell. The sp. gr. of the fused nitride is 6·93. A. E. van Arkel made observations on this subject. The m.p. is 2930°, and it does not sublime before melting. The electrical resistance is $1{\cdot}6\times10^{-4}$ ohm at ordinary temp. and $3{\cdot}2\times10^{-4}$ at the m.p. E. Wedekind obtained **zirconium hemitrinitride**, Zr_2N_3, by the reduction of zirconium by magnesium in an open crucible; and removed the zirconia by flotation in tribromomethane. J. M. Matthews also prepared it by heating zirconium tetrachloride to redness in dry ammonia. J. M. Matthews' product was an amorphous, dark grey powder; while under the microscope, E. Wedekind's product appeared as bronze-coloured crystals with a green shimmering lustre. The sp. gr. was 6·75 at 15°. K. Becker and F. Ebert found the X-radiogram corresponded with an elementary cube of side 4·63 A., and density 6·97; A. E. van Arkel gave 4·59 A. for the side of the cube. The compressed powder is an electrical conductor. There is no perceptible dissociation of the nitride at 1100°; and it is not affected by heating to redness in a current of hydrogen, but at 1050°, ammonia begins to be formed—in the converse reaction, nitrogen acts on the hydride also forming ammonia. When heated in air, it glows with the formation of zirconia. At a red-heat, the nitride reacts with chlorine or bromine with incandescence; it is more resistant to oxygen and chlorine than is the metal. It is very stable towards acids—excepting hydrofluoric acid which decomposes the nitride giving off ammonia gas. Aq. soln. of the alkali hydroxides do not act on the nitride; but with fused potassium hydroxide, ammonia is evolved.

C. Matignon[16] prepared **cerium nitride**, CeN, by reducing the oxide with magnesium or aluminium in an atm. of nitrogen; or the chloride with sodium in an atm. of nitrogen. A. C. Vournasos prepared it by adding the powdered metal to fused potassium cyanide as in the case of boron nitride; and J. Lipsky, by the action of ammonia on the hydride. W. Muthmann and K. Kraft found that cerium at a moderate red-heat acts but slowly on nitrogen, but at 850°, there is a sudden and violent reaction, the formation of the nitride being accompanied by a brilliant incandescence. If the nitrogen contains a small proportion of oxygen or nitrogen oxides, the product is dark grey, and contains an oxide; but with purified nitrogen, the nitride is bronze-coloured, almost black. G. Tammann measured the rate of formation of nitride when cerium is heated in nitrogen. On the other hand, F. W. Dafert and R. Miklauz said that the nitride cannot be obtained from its elements, but is formed by heating the hydride in nitrogen at 800°–900°. E. Friederich and L. Sittig obtained a trace of the nitride by heating a mixture of the oxide and carbon at 1250°. F. Fichter and C. Schölly observed that when cerium carbide is heated in nitrogen it does not behave like calcium nitride at 1250°, and form cyanide or cyanamide, but rather forms cerium nitride, CeN. Cerium carbide also reacts with ammonia at 1250°, yielding the nitride, but the action is slower and less complete than is the case with nitrogen. A. C. Vournasos said that the nitride is easily oxidized in air, and consequently he was not able to eliminate carbon by ignition in air. J. Lipsky found the dissociation press. to be immeasurably small at 320°; between 6 mm. and 13 mm. at 460°; 340 mm. at 610°; 370 mm. at 675°; 380 mm. at 715°; and 400 mm. at 762°. The data are only approximate because equilibrium is attained very slowly—due to the equilibrium being quickly established on the surface, the nitride then dissolving in the metal, and further change being then dependent on diffusion in the solid. The change was not accelerated by admixtures of alkali or alkaline earth chlorides. Purified and dried nitrogen when passed over the freshly prepared hydride in the cold, reacts quickly, forming ammonia; the reaction, $CeH_3+N_2 \rightleftharpoons CeN+NH_3$, quickly slows down owing to the formation of a protective superficial film of nitride. Raising the temp. 200° accelerates the reaction very little. No ammonia is formed by the action of hydrogen on cerium nitride in the cold, but between 100° and 400° —preferably 200°—ammonia is formed: $CeN+3H_2 \rightleftharpoons NH_3+CeH_3$. F. W. Dafert and R. Miklauz said that ammonia is not formed by the action of hydrogen on the heated nitride. J. Lipsky found that a mixture of hydrogen and nitrogen gases acting on cerium nitride at 25° furnishes ammonia. The catalytic reaction stops in about 24 hrs., possibly owing to the presence of moisture and oxygen in the mixed gases. The continuous production of ammonia soon stops if a mixture of nitrogen and hydrogen is used, but it goes on continuously (although slowly) when nitrogen and hydrogen are passed alternately at short intervals. A mixture of hydride and nitride gives the best results, and the rate of production is very much increased by spreading the material out over a large surface of asbestos, glass wool, or copper gauze. When the contact material is allowed to cool off and remain unused for some hours, its activity increases. The quantity of ammonia produced is proportional to the quantity of contact material used, and independent, within fairly wide limits, of the rate of passage of the gas. The highest conc. of ammonia reached was 6·4 per cent. by vol. in the gas passed over cerium nitride; and 1·4 per cent. over the hydride. N. Woodhouse, and J. Lipsky made some observations on the fixation of nitrogen as ammonia *viâ* cerium nitride as intermediary. W. Muthmann and K. Kraft said that the nitride suffers no change in dry air, but in contact with moisture, ammonia is evolved; the mass finally becomes hot and glows as it is oxidized to ceric oxide. The reaction with water is violent; and if a few drops of water be sprinkled on the nitride, the mass becomes bright red as it is converted into ceric oxide—ammonia and hydrogen are evolved and burn: $2CeN+4H_2O=2CeO_2+2NH_3+H_2$. The nitride dissolves quietly in an aq. soln. of potassium hydroxide, forming cerous hydroxide and ammonia. With dil. acids the dissolution is accompanied by the formation of cerous and ammonium salts: $2CeN+4H_2SO_4=Ce_2(SO_4)_3+(NH_4)_2SO_4$. The reaction with dil. acids is sometimes so violent that the mass becomes incandescent, and at the high temp., some ammonia is decomposed into its elements. According to P. Fabaron, when metallic cerium is heated in a closed copper tube, the oxygen of the air in the tube combines with the copper and the nitrogen with the cerium. The **cerium dinitride,** CeN_2, formed has a greyish-black colour and is decomposed by water, yielding ammonia and cerous oxide.

According to J. J. Chydenius,[17] thorium oxide is not changed when heated in ammonia; but if thorium tetrachloride alone or mixed with ammonium chloride is heated in ammonia gas, a white insoluble powder is formed which gives off ammonia when fused with potassium hydroxide. E. Chauvenet obtained what appeared to be thorium nitride by heating thorium tetramminotetrachloride at a red-heat. E. Friederich and L. Sittig obtained the impure nitride by heating a mixture of the oxide and carbon in a current of nitrogen. H. Moissan and A. Étard made **thorium nitride,** presumably Th_3N_4, by heating the carbide at 500° in an atm. of ammonia. A. E. van Arkel and J. H. de Boer made thorium nitride by the process they used for titanium nitride. C. Matignon made this compound by heating a mixture of thorium dioxide and magnesium in an atm. of nitrogen; and C. Matignon and M. Delépine, by heating thorium in nitrogen gas—since the absorption by thorium itself is slow, thorium hydride can be used. The dark brown nitride is not altered at a red-heat. It burns in air with incandescence; and in oxygen, the incandescence is very vivid, being probably due to thorium. Cold water decomposes the nitride slowly; hot water, rapidly, forming thorium hydroxide and ammonia. Dil. acids decompose the nitride, forming ammonium and thorium salts; and with alkali-lye, ammonia is formed.

V. Kohlschütter prepared what he called *thorium metanitride,* a polymer of the tetratritanitride, by heating a mixture of thoria and magnesium to a high temp. in the presence of nitrogen. The citron-yellow product is less reactive than the tetratrinitride just described. It is said to be insoluble in conc. and dil. acids, and with water, to form hydrogen. It is attacked when heated in oxygen, or chlorine; and when fused with alkali hydroxide. C. Matignon and M. Delépine consider it to be an oxynitride, $Th_4O_5N_2$.

K. Iwase[18] found out tin does not dissolve nitrogen. G. G. Henderson and J. C. Galletly heated tin in ammonia from 160° to redness, and found that the metal retained no marked amount of nitrogen; from 170°, the metal became matte, and showed rounded globules when viewed under the microscope. When the temp. approached redness, the ammonia was decomposed by the metal. It was assumed that an unstable nitride was formed. F. Fischer and co-workers prepared an impure **tin nitride,** by the method indicated in connection with Fig. 11. When treated with cold hydrochloric, sulphuric, phosphoric, or oxalic acid, the nitride is not changed, but with hot hydrochloric, sulphuric, or phosphoric acid, the mass is dissolved. There is only a slight reaction with cold conc. nitric acid; boiling conc. nitric acid attacks it only slowly; the dil. acid, cold and hot, attacks the preparations more. G. G. Henderson and J. C. Galletly found the action of nitrogen on lead resembled its action on tin. P. Herrmann found that ammonia reduces lead chloride at 500°–600° to lead; and at 0°–250°, spongy lead absorbs no nitrogen. F. Fischer and F. Schröter reported an impure **lead nitride** to be formed by the method given in connection with Fig. 11. The product was said to be very unstable, and explosive; and to yield an ammonium salt with acids. W. Beltz discussed the stabilization of lead nitride.

According to H. B. Baker and H. B. Dixon,[19] red phosphorus heated to 300° in a stream of nitrogen suffers no change. A. Stock and H. Grüneberg also obtained no phosphorus nitride by the action of nitrogen or ammonia gas on phosphorus. If a very high temp. were employed, there might be a reaction. W. P. Winter reported that when sodamide is warmed with yellow phosphorus, an energetic reaction occurs, and the product is a mixture of sodium phosphide, oxy-acids of phosphorus, and probably a phosphorus amide. According to H. Schiff, the phosphorus nitride reported by H. Rose, and F. Wöhler and J. von Liebig, is probably phospham, PN_2H. W. H. Balmain reported a phosphorus nitride, of undetermined composition, to be formed by the action of phosphorus on hot mercuric chloroamide. W. Moldenhauer and H. Dörsam found that when yellow phosphorus is distributed as evenly as possible over the inside of a glass tube, it readily absorbs nitrogen at 180–200 mm. press. when exposed to electric discharges between aluminium electrodes. The product is a mixture of unchanged white phosphorus, red phosphorus, and **phosphorus mononitride,** PN. It is extracted with carbon disulphide, and the residue is heated in a porcelain boat in a slow current of nitrogen at 500°–550° and 12 mm. press.; the nitride thus acquires some impurities from the porcelain. It is a voluminous, yellowish-brown powder, extraordinarily resistant to chemical agents.

According to A. Besson, when phosphamide is heated in a current of nitrogen in a porcelain tube at a high temp., the end-product of the reaction corresponds with *phosphorus mononitride*, PN. A. Stock and H. Grüneberg, however, were unable to find any nitride other than P_3N_5.

F. Briegleb and A. Geuther prepared *phosphorus tritapentanitride*, or **phosphorus nitride,** P_3N_5, by passing the vapour of phosphorus pentachloride accompanied by nitrogen over heated magnesium nitride: $5Mg_3N_2+6PCl_5=15MgCl_2+2P_3N_5$; and E. A. Schneider's nitride obtained by using phosphorus trichloride is probably the same compound. A. Stock and B. Hoffmann obtained this same nitride by heating the products of the action of dry ammonia on phosphorus pentasulphide at 230°; and by heating ammonium iminotrithiophosphate, $(NH_4S)_3PNH$, in a current of ammonia. A. Stock made it by heating iminotrithiophosphoric acid, $HNP(SH)_3$; ammonium nitrilodithiophosphate, $(NH_4S)_2PN$; thiophosphoric nitrile, NPS; and by heating phosphorus pentasulphide in a current of ammonia at 850°. The purified pentasulphide was first sat. with dry purified ammonia at ordinary temp., and the product heated in an atm. of ammonia till the Jena glass containing tube began to soften; the complex mixture of ammonium thiophosphates so obtained was heated for 12 hrs. at 850° in a current of ammonia, or the products of its decomposition. Phosphorus nitride of a high degree of purity remained. A. Stock and H. Güneberg found that phosphorus heptasulphide gave a poor yield, and phosphorus trisulphide none. The product obtained by heating a mixture of pentasulphide and ammonium chloride is impure. A. Stock and co-workers found that the nitride is formed among the products of the action of liquid ammonia on ordinary phosphorus or phosphorus dihydride, P_4H_2; or by heating the ammino-compounds of solid phosphorus hydrides.

Phosphorus nitride is without taste or smell. Its colour may be white, or may vary from white to dark red according to the time it has been heated above 850°. The film of red phosphorus sometimes observed on the surface has no perceptible influence on its composition. A. Stock and H. Grüneberg gave for the sp. gr. at 18° the value 2·51; H. Herzer, 2·495 for the sp. gr. at 25°/4°; 65·2 for the mol. vol.; and 910° for the temp. of decomposition; and A. Stock and F. Wrede, +81·5 Cals. for the heat of formation per mol of P_3N_5 from ordinary phosphorus, and +70·4 Cals. from red phosphorus; the mol. heat of combustion is 473·2 Cals. at constant vol., and 474·7 Cals. at constant press. A. Stock and B. Hoffmann could find no solvent for the nitride. A. Stock and H. Grüneberg said that the nitride is chemically inactive at ordinary temp., but at a high temp. it acts as a powerful reducing agent in consequence of its dissociation into phosphorus and nitrogen which begins in vacuo at 760°. According to A. Stock and co-workers, when the nitride is heated to redness in *hydrogen* it furnishes phosphorus and ammonia; it burns when heated in *oxygen;* at ordinary temp. *water* has little or no action, while boiling water slowly decomposes it into ammonia and phosphoric acid: $P_3N_5+12H_2O=3H_3PO_4+5NH_3$; F. G. Liljenroth proposed to utilize this reaction in the manufacture of ammonia. The decomposition by water in a sealed tube at 180° is quantitative after a few hours' action. Aq. soln. of all kinds, including conc. *nitric acid*, have no action. When heated in *chlorine*, the nitride takes fire at the temp. of softening glass. When heated with many *metals*—*e.g.* magnesium—phosphides are formed. It reduces *metallic oxides*—*e.g.* lead oxide at a dull red-heat gives lead; and arsenic trioxide, arsenic; the reduction of antimony trioxide proceeds with difficulty; and zinc oxide, at the softening temp. of glass, is not changed.

I. A. Bachman[20] found that no signs of **arsenic nitride,** AsN, were obtained by heating arsenic trioxide to 300°–350° in an atm. of ammonia; but if a sealed tube containing silver cyanide and arsenious oxide be heated at this temp., a dark brown substance is formed as a coating over the crystals of arsenic trioxide. The brown substance contained only a little carbon, and was considered to be the impure nitride. F. Fischer and F. Schröter prepared arsenic nitride by the process indicated in connection with Fig. 11. C. Hugot prepared arsenic nitride by rapidly heating arsenic imide in vacuo at 250° : $As_2(NH)_3=2AsN+NH_3$. The orange-red product is decomposed into its elements at a temp. not far distant from its temp. of formation. I. A. Bachman said that the nitride gives off ammonia when heated with soda-lime; it dissolves partially in alkali-lye; and dissolves completely in strong acids. F. Hérard [21] found that when antimony is heated to dull redness in a current of nitrogen, greyish vapours are evolved. K. Iwase found that nitrogen is not dissolved by antimony. E. C. Franklin [22] reported an impure antimony nitride to be formed by the action of antimony iodide on potassium amide in liquid ammonia soln. which condenses on the cool parts of the tube in agglomerations of amorphous antimony. The fact that the amorphous variety of antimony is not produced in a current of nitrogen is taken to indicate that **antimony nitride,** SbN, is formed which decomposes in the cooler parts of the tube. F. Fischer and F. Schröter obtained the impure nitride as a black powder by the method indicated in connection with Fig. 11. The nitride decomposed explosively when heated depositing a mirror of antimony on the containing tube. When treated with dil. hydrochloric acid, antimony and ammonium chlorides were formed: $SbN+4HCl=SbCl_3+NH_4Cl$. F. Fischer and co-workers prepared **bismuth nitride,** BiN, by the method indicated in connection with Fig. 11. E. C. Franklin prepared it by the action of bismuth tribromide or triiodide on potassamide in liquid ammonia soln.: $BiI_3+3KNH_2=BiN+3KI+2NH_3$. The dark brown precipitate becomes almost black on drying, and gradually decomposes on standing—when the dry precipitate is heated with dil. hydrochloric acid some bismuth always remains. The dry nitride explodes when treated with water or dil. acids. It is slowly decomposed by water vapour. F. Fischer and F. Schröter said that explosion occurs when the dry nitride is shaken and the walls of the containing tube become covered with a mirror of bismuth.

H. E. Roscoe [23] showed that what J. J. Berzelius had reported to be metallic vanadium was really a nitride. Three nitrides have been reported, V_2N, VN, and VN_2. There is a doubt whether or not the first two substances are the same. H. Mehner obtained the nitride by heating a mixture of carbon and vanadium oxide in an atm. of nitrogen. I. I. Shukoff observed no reaction between nitrogen and vanadium at 1250°. G. Tammann noted the formation of a film of nitride when vanadium is heated in nitrogen; and C. Setterberg obtained an impure nitride during the electrolysis of a soln. of ammonium vanadate. H. E. Roscoe prepared **vanadium mononitride,** VN, by passing ammonia over vanadyl trichloride contained in a bulb tube and heated until all the ammonium chloride had been expelled; the remaining black powder was heated to whiteness in a platinum boat in a current of ammonia for several hours. It was also obtained by heating for a long time ammonium vanadate to whiteness with the exclusion of air; by heating vanadium trioxide to whiteness in a current of ammonia; and by heating vanadium in nitrogen. E. Friederich and L. Sittig made it by heating the oxide in hydrogen and nitrogen gases; and A. E. van Arkel, by heating the metal filament in an atm. of nitrogen. The greyish-brown powder is not altered at ordinary temp. in air, but when heated, it forms blue vanadium oxide, VO_2, and at a higher temp., vanadium pentoxide. It loses nitrogen when heated in hydrogen; and evolves ammonia when heated with soda-lime. N. Whitehouse, however, found that at 400°, water vapour forms ammonia and vanadium oxide. K. Becker and F. Ebert found that the X-radiogram corresponded with a cube of side 4·28 A., and density 5·46. E. Friederich and L. Sittig found the space-lattice is a face-centred cube of the sodium chloride type with side 4·28 A. There are four mols. per unit cell. The sp. gr. is 5·63; the m.p. is about 2050°; and it decomposes but does not sublime at the m.p. R. E. Slade and G. I. Higson said that the dissociation press. of vanadium nitride at 1203° does not exceed 0·2 mm., and at 1271° does not exceed 1·5 mm. The respective heats of formation are 79·2 Cals. and 77·2 Cals. The electrical resistance is 2×10^{-4} ohm at ordinary temp., and $8{\cdot}5\times10^{-4}$ ohm at the m.p. E. Wedekind and C. Horst gave $4{\cdot}13\times10^{-6}$ for the magnetic susceptibility.

W. Muthmann and co-workers also reported that finely divided vanadium reacts with nitrogen at a red-heat. The reaction is so slow that 20–24 hrs. are needed for the increase in weight to become constant; nitrogen is also absorbed at dull redness, but the action is still slower. In contradistinction to H. E. Roscoe, the composition of the product approximated **vanadium heminitride,** V_2N. R. E. Slade and G. I. Higson found that vanadium nitride dissociates at 1203° and 0·2 mm. press. According to N. Whitehouse, at a white-heat vanadium forms the mononitride. The velvety-black powder is unchanged in air; when heated in air, however, it forms vanadium pentoxide; water, and dil. hydrochloric acid, hot or cold, have no action, but it dissolves in cold dil. nitric acid. G. Gore found that vanadium nitride is insoluble in liquid ammonia. It is not affected by alkali-lye, but with fused potassium hydroxide, ammonia is evolved.

In 1858, **vanadium dinitride,** VN_2, was prepared by E. Uhrlaub, but a wrong formula was given to it owing to an erroneous value for the at. wt. having been used in calculation. Both H. E. Roscoe, and E. Uhrlaub obtained it by heating vanadyl chloride in a current of dry ammonia until most of the ammonium chloride had volatilized, as in the case of the mononitride, but instead of raising the temp. to whiteness, the product was washed in ammoniacal water, and dried in vacuo over conc. sulphuric acid. The black powder so obtained loses nitrogen when heated, and passes into the mononitride; when exposed to air, ammonia is evolved and the vanadium is oxidized. With molten potassium hydroxide, ammonia is developed; sodium hydrochlorite gives nitrogen; nitric acid in the cold does not attack this nitride, but when heated the attack is vigorous. E. Uhrlaub, and A. Safarik found about 0·1 per cent. of hydrogen in the compound.

H. Moissan[24] found that when powdered columbium is heated to 1200°, in nitrogen, the metal becomes coated with yellow *niobium nitride* or **columbium tritapentanitride,** Cb_3N_5, but at 500°–600°, there is no perceptible action. L. Weiss and O. Aichel observed that when columbium is heated in air, both oxide and nitride are formed. H. Moissan also observed that finely powdered columbium dissociates ammonia at a red-heat without changing in weight; and W. von Bolton showed that when columbium is heated in ammonia, the metal becomes matte and greyish-brown, and gives off ammonia when heated with potassium hydroxide, showing that some nitride was formed. H. Rose prepared a nitride by heating columbyl chloride in a current of ammonia. A. Joly said that this product shows all the properties of a mixture of columbic oxide and nitride. H. St. C. Deville, H. Rose, and A. Joly found that a nitride corresponding, according to H. St. C. Deville, with **columbium mononitride,** CbN, is formed when columbic oxide is heated to a high temp. in a current of ammonia. E. Friederich and L. Sittig obtained the mononitride by heating a mixture of the oxide and carbon in nitrogen gas; and they said that the space-lattice is a face-centred cube of the sodium chloride type with side 4·41 A., and four mols. per unit cell. The sp. gr. is 8·4; the m.p. 2050°, and it decomposes but does not sublime at the m.p. E. Friederich gave 3070° for the m.p. W. Muthmann and co-workers obtained the pentatritanitride by heating the hydride to redness in a current of nitrogen. R. D. Hall and E. F. Smith obtained the pentatritanitride by the action of dry ammonia on an ethereal soln. of columbium pentachloride. K. Becker and F. Ebert found the X-radiogram corresponded with an elementary cube of side 4·41 A., and density 8·26. W. Muthmann and co-workers found that the pentatritanitride is a black powder which is stable in air, but burns when heated, forming columbium pentoxide. The nitride is not attacked by boiling water; nor is it decomposed by nitric acid, conc. sulphuric acid, or hot hydrochloric acid—it is only attacked by acids which can dissolve columbium. Boiling alkali-lye does not attack the nitride, but with fused potassium hydroxide, at dull red-heat, ammonia is evolved.

According to A. Sieverts and E. Bergner, tantalum nitride is slowly formed when tantalum is heated in nitrogen gas above 900°; but G. Tammann observed no reaction between nitrogen and tantalum at 700°. A. Joly, and H. Rose also obtained a nitride of undetermined composition by the prolonged action of ammonia on tantalum pentoxide. A. Joly reported **tantalum tritapentanitride,** Ta_3N_5, to be formed when ammonia is passed for some time into cold tantalum pentachloride, and heating the product up to a temp. sufficient to volatilize the ammonium chloride. The amorphous red powder when heated in air quickly forms tantalum pentoxide; when heated with cupric oxide, copper and nitrogen are formed; and when fused with potassium hydroxide, ammonia is evolved. A. Joly showed that if this nitride is heated to whiteness in a current of ammonia, nitrogen is evolved and black **tantalum mononitride,** TaN, is formed. E. Friederich and L. Sittig made it by heating the oxide in a current of nitrogen and hydrogen; and A. E. van Arkel, by heating a filament of the metal in nitrogen. K. Becker and F. Ebert found that the X-radiogram corresponded with hexagonal symmetry and an elementary parallelopiped of side 3·61 A.; A. E. van Arkel gave 3·05 A., and for the axial ratio $a : c = 1 : 1{\cdot}62$. According to W. Muthmann and co-workers, **tantalum dinitride,** TaN_2, is formed when the metal is heated in nitrogen gas to 1000°. R. E. Slade and G. I. Higson found that the dissociation press. of tantalum nitride, at 1170°, is 0·4 mm.; and the heats of formation, 74·7 and 79 Cals. respectively. The properties of tantalum nitride resemble those of columbium pentatritanitride.

According to H. St. C. Deville,[25] **columbium carbonitride,** mCbN.nCbC, is formed when sodium columbate is heated to 1200° in a graphite crucible. A. Joly made it by heating a mixture of columbium pentoxide, carbon, and sodium carbonate (4 : 1 : 1) in a carbon crucible at a high temp.; and by the action of ammonium cyanide on columbium pentoxide at a high temp. The analyses of A. Joly varied from $m : n = 2 : 3$ to $1 : 5$. The greyish-violet or olive-green mass of acicular crystals burns in air or oxygen at a high temp.; chlorine transforms it into columbium pentachloride, carbon tetrachloride, and carbon—not columbium oxytrichloride; copper or lead oxide is vigorously reduced. H. Rose found that freshly prepared, hydrated columbium pentoxide, when heated to redness in cyanogen, furnishes black pulverulent **columbium oxycarbonitride,** $Cb_2O_5N_5C$. It conducts electricity well; it oxidizes slowly when heated in air; and gives off ammonia when treated with fused potassium hydroxide.

For *sulphur nitride,* see nitrogen sulphide; for *selenium nitride,* see nitrogen selenide; and for *tellurium nitride,* see nitrogen telluride. J. von Liebig[26] obtained a brown powder by igniting chromium chloride in ammonia, and he thought the product was elemental chromium. A. Schrötter showed that the product is **chromium nitride,** Cr_2N_2 or CrN.

According to A. Schrötter, the chromic chloride should be prepared as free as possible from oxide, and from water by heating it in a glass tube on an oil-bath until no more water is evolved. The tube is then cooled, and ammonia passed for a time. The tube is then heated, and ammonia passed until no more ammonium chloride is evolved. The cold mass is removed from the tube, crushed to small fragments, and again treated with ammonia. This operation is repeated several times.

A. Schrötter obtained a similar product by the action of ammonia on chromochloric acid, and C. E. Ufer said that the product then contains oxygen. H. N. Warren, E. Oliveri-Mandala and G. Comella, R. Kraus, C. E. Ufer, and E. Uhrlaub also prepared the nitride by the action of ammonia on chromic chloride; and the two last-named also made it by heating a mixture of ammonium and chromic chlorides: $CrCl_3 + NH_4Cl = 4HCl + CrN$. According to C. E. Ufer, if potassium dichromate, mixed with ammonium chloride, be melted under a layer of sodium chloride, only chromic oxide is formed; but G. B. Frankforter and co-workers said that a nitride is probably formed. F. Briegleb and A. Geuther obtained this nitride by heating chromium in an atm. of nitrogen;

and J. Férée, by heating pyrophoric chromium in an atm. of nitrogen. H. Hardtung gave 1200° for the temp. of formation. G. Tammann made some observations on the reaction. E. Baur and G. L. Voerman found that the reaction $2Cr+N_2\rightleftharpoons 2CrN$ is reversible. H. Herzer found the sp. gr. to be between 5·796 and 5·800 at 25°/4°; and the mol. vol. 11·4. E. Baur and G. L. Voerman found on heating the nitride at 790° ± 10°, the press., p mm., to be:

	0	3	9	21	37	59	180	4140 mm.
p .	174·5	172·5	170·5	166·5	152	157	139·5	126 mm.

They did not measure the dissociation press. at higher temp., and added that the dissociation does not proceed until a definite dissociation press. has been attained and then ceases as is commonly the case; rather does the dissociation press. exhibit a continuous slow change. This is explained by assuming that chromium and its nitride form not two phases, but only one variable phase. J. Férée made the nitride contaminated with a little oxide by heating pyrophoric chromium in a current of nitric oxide; and he also obtained this nitride by the action of ammonia on heated chromium.

E. Uhrlaub said that **chromium tritadinitride**, Cr_3N_2, is formed by heating the mononitride, CrN, in a current of ammonia; and G. G. Henderson and J. C. Galletly, reported this same oxide by heating chromium in ammonia at 850°. It was said to be black, and very indifferent towards chemical agents. It is oxidized when heated in air, or when melted with sodium dioxide. Nitric acid or aqua regia attacks it slowly.

A. Smits obtained the mononitride, CrN, by the action of chromic chloride on magnesium nitride; and A. Guntz, by the action of potassium chlorochromate on lithium nitride. Chromium nitride is a brown or black amorphous powder which C. E. Ufer found partially to decompose into its elements at about 1450°. E. Wedekind and T. Veit said that the nitride is not affected by an ordinary horse-shoe magnet, but is affected by a large electromagnet. I. I. Shukoff showed that the electrical conductivity of the powdered nitride, 12·72 to 15·40 mhos, is of the same order as that of the metals, and he therefore concluded that the so-called nitrides are only solid soln. of nitrogen and chromium, and not true chemical compounds. E. Baur and G. L. Voerman observed that chromium nitride is a very efficient catalytic agent in the decomposition of ammonia, whilst it has no effect in promoting the synthesis of ammonia. Hence, it was called a one-sided catalyst—*ein einseitiger Katalysator*. E. Baur and G. L. Voerman said that chromium nitride is much more stable than iron nitride, and is not reduced by *hydrogen*, even at 560°, 13 atm. press. C. E. Ufer found that when heated to redness in *air*, the nitride oxidizes with incandescence to form green chromic oxide; and A. Schrötter, and C. E. Ufer showed that it inflames in *oxygen* at 150°–200°, and burns to chromic oxide with a red light and the evolution of nitrogen. A. Briegleb and A. Geuther's nitride burned with difficulty in oxygen. C. E. Ufer said that the nitride is not attacked by *water*, or steam at 220°. It is not attacked by cold *chlorine*, but when heated in that gas, there are some small detonations at the beginning attributed to the possible formation of nitrogen chloride—a brownish-black sublimate, and violet chromic chloride, while nitrogen is evolved. Dry *hydrogen chloride* at a red-heat acts slowly without the evolution of a gas: $CrN+4HCl=CrCl_3+NH_4Cl$. An aq. soln. of an *alkali hypochlorite* reacts in the cold, forming an alkali chromate, and nitrogen; the nitride mixed with *potassium chlorate* detonates violently when heated. Dil. *acids*, and hot or cold conc. *nitric, hydrochloric, and hydrofluoric acids* are without action; boiling *aqua regia* dissolves it with difficulty; conc. *sulphuric acid* reacts slowly without the evolution of a gas, forming red chromic and ammonium sulphates. Dil. hot or cold *alkali-lye* has no action on the nitride; and when fused with *potassium hydroxide* at 190°, in a sealed tube, it forms only a trace of chromate, and gives off no ammonia. J. Férée said that when heated with *soda-lime* it gives off ammonia. C. E. Ufer found that the nitride could be heated for many hours with melted *sodium carbonate* in a covered crucible without change—if air has access, traces of chromate are formed. It detonates in contact with molten *potassium nitrate* giving off nitrogen but no red fumes.

F. Wöhler[27] obtained a **molybdenum nitride** of undetermined composition by heating together a mixture of ammonium and molybdenum chlorides. The black product gave off ammonia when treated with fused potassium hydroxide. G. G. Henderson and J. C. Galletly found that molybdenum reacts with ammonia at 850°, more slowly than chromium, and only a small proportion of a nitride is formed; and I. I. Shukoff observed a slight absorption of nitrogen at 780°; but G. Tammann observed none at 700°. W. Lederer obtained a molybdenum nitride from an arc between molybdenum electrodes in an atm. of nitrogen or of ammonia. The Badische Anilin- und Soda-fabrik heated molybdenum oxy-compounds in the presence of reducing gases mixed with nitrogen under press., and obtained the nitride—*e.g.* molybdenum trioxide at 500°–600° in an atm. of equal parts of nitrogen and hydrogen under 60 atm. press. I. Langmuir also observed that when a molybdenum filament is heated to about 2000°–2400° K., in nitrogen at 0·03 mm. press., the filament loses weight, and the nitrogen disappears. A deposit of molybdenum containing nitrogen collected on the walls of the bulb. The rate of disappearance of the nitrogen is independent of the press. when the latter exceeds one bar; the amount of nitrogen thus disappearing is much less than the chemical eq. of the molybdenum evaporated, and the ratio, ϵ, of the number of mols. of nitrogen removed to the number of atoms of molybdenum evaporated in the same time decreases from a maximum of about 0·4 to a minimum of about 0·01 as the temp. of the filament or bulb is raised. With very minute press. of water-vap., such as result even in presence of drying agents from failure to "bake out" the bulb, no complete removal of nitrogen occurs, although under such conditions molybdenum will remove carbon monoxide and tungsten will remove either nitrogen or carbon monoxide, the value of ϵ in each of these cases being unity. The fact that ϵ is independent of the press., but dependent on the filament and bulb temp., indicates that the reaction occurs in the space around the filament, and that each collision between molybdenum atoms and nitrogen mols. results in combination, at least two products being formed; these are probably a first-order compound of the formula NMoN and a second-order compound, $Mo : N_2$, the proportion between the amounts of these two depending on the relative velocity of the mols. at the moment of collision and on the internal velocity of the nitrogen mols. The former compound is very stable and cannot be decomposed on the bulb by heating to 360°, its formation being favoured by low relative translational velocity of the colliding mols. and by high internal or rotational velocity in the nitrogen mol. All those collisions which do not yield a first-order compound give one of the second order which is so unstable that it decomposes practically completely on striking the bulb, owing to the attractive forces between pairs of molybdenum atoms being much greater than between these and nitrogen mols. The deposit which collects on the bulb has the following properties. It is spongy and can easily be rubbed off with the finger on opening the bulb, whereas deposits formed in a high vacuum are dense and can scarcely be scratched off with a knife. If the bulb is kept at the temp. of liquid air, the deposit formed gives up some nitrogen when warmed to the ordinary temp., but only part of this nitrogen is absorbed again on cooling the bulb; the larger part of the nitrogen in the deposit is not, however, liberated by heating in a vacuum at 360°. The deposit very rapidly absorbs up to about one-thirteenth of its chemical eq. of nitrogen when cooled by liquid air, but it does not readily absorb hydrogen under these conditions. At the ordinary temp., or above, however, large quantities of hydrogen are absorbed or dissolved by the deposit, these being given up slowly at 300° in a good vacuum. When heated in nitrogen at 270° or above, the deposit combines with nitrogen, and this is not given off again at 360° in a vacuum. The deposit reacts rapidly with water-vap., at the ordinary temp. with production of hydrogen, much of which remains dissolved in the deposit until liberated by heating at 360° in vacuo. It is probable that the molybdenum is in an atomic state of division as a result of being deposited atom by atom by the decomposition of the unstable compound formed in the "unsuccessful collisions." Molybdenum deposited on the bulb in a high vacumu does not exhibit any of these characteristics. A. Rosenheim and H. J. Braun prepared **molybdenum tritadinitride,** Mo_3N_2, by heating molybdenum trichloride in ammonia at 760°; and E. Uhrlaub, by heating molybdenum trichloride in dry ammonia on a gradually rising temp. The analyses of the greyish-black product corresponded with **molybdenum pentitatrinitride,** Mo_5N_3; and after heating to a higher temp., the composition corresponded with **molybdenum pentitatetranitride,** Mo_5N_4. E. Uhrlaub using an old at. wt. determination represented the composition Mo_3N_2. At a white-heat, the end-product is molybdenum. H. Herzer gave 8·036 to 8·046 for the sp. gr. of Mo_3N_2 at 25°/4°; and 39·3 for the mol. vol.

According to F. Wöhler,[28] a black, pulverulent tungsten nitride is formed when the vapours of tungsten and ammonium chlorides are passed through a red-hot tube; and also when tungsten trioxide is heated in cyanogen. I. I. Shukoff observed no absorption of nitrogen by tungsten at 1250°; and G. Tammann, none at 700°. I. Langmuir observed similar phenomena with tungsten filaments at 3000° K. as those observed in the case of molybdenum filaments. When a tungsten lamp containing nitrogen, at a low press., is run for some time the nitrogen gradually disappears, and the disappearance is brought about in three ways: (i) Chemically by the formation of **tungsten dinitride,** WN_2; (ii) Electrochemically—when an electric discharge passes through nitrogen and a hot tungsten cathode is used, the nitride WN_2 is formed at the cathode; (iii) Electrically—at very low press. and high voltages there seems to be a reversible removal of limited quantities of nitrogen, in which the nitrogen is driven on to the glass in such a form that it can be recovered by heating. From zero press. up to about 0·001 mm. the rate of removal of the nitrogen is proportional to the product of the rate of evaporation and the press. of nitrogen. From about 0·003 mm. up to about 1 mm., the rate is directly proportional to the rate of evaporation, and independent of the press.; above press. of 2 mm., there is still direct proportionality between the rate of removal and the rate of evaporation, but the latter is materially reduced by the presence of the gas. The nitride, WN_2, in thin layers is a clear, brown colour, very different in appearance from finely divided tungsten. C. J. Smithells and H. P. Rooksby gave 6·3 for the sp. gr. The dinitride is stable in a vacuum at 400°, but is decomposed at 2400° K. It is decomposed by water, giving ammonia and probably the oxide WO_3. Nitrogen does not, at any temp., react perceptibly with solid tungsten. The behaviour of nitrogen towards solid tungsten and tungsten vapour is similar to that of oxygen towards platinum and platinum vapour. G. G. Henderson and J. C. Galletly found that heated tungsten decomposes ammonia, but virtually no nitride is formed. H. Hardtung gave 1365° for the temp. of formation. R. Pörscke and A. Rathjen observed the formation of a nitride when the tungsten filament of an electric lamp is heated in ammonia. E. Uhrlaub reported the formation of **tungsten tritadinitride,** W_3N_2, when tungsten tetrahydrohexanitride, $W_3N_6H_4$, is heated in ammonia; and S. Rideal, **tungsten hemitrinitride,** W_2N_3, by heating tungsten chloride or oxychloride in ammonia. The black, lustrous powder can be freed from ammonium chloride by washing. H. Herzer gave 12·083 to 12·120 for the sp. gr. at 25°/4°; and 33·8 to 33·9 for the mol. vol. When heated in air, this nitride furnishes tungsten trioxide. Conc. sulphuric acid oxidizes it to tungstic acid and ammonium sulphate. It is insoluble in nitric acid, dil. sulphuric acid, and soda-lye; it gives off ammonia when treated with fused potassium hydroxide; and aqua regia oxidizes it to tungstic oxide.

C. F. Rammelsberg[29] found that dry ammonia reduced uranium tetrachloride to the trichloride, giving off nitrogen; and E. Uhrlaub showed that if the tetrachloride be heated for some hours in ammonia gas, and finally in the vapour of ammonium chloride, a black nitride was formed. A. Colani also noted that if sodium chlorouranate be heated to redness in dry ammonia, a black crystalline nitride is formed. H. Moissan found that uranium unites directly with nitrogen at 1000°, or with ammonia at a lower temp., forming a yellow **uranium tritatetranitride,** U_3N_4. The same product was obtained by heating uranium carbide to 1100°, but the reaction was incomplete. E. Friederich and L. Sittig prepared uranium nitride in an impure state by heating a mixture of the oxide and carbon in nitrogen. V. Kohlschütter prepared uranium chloride by the action of chlorine on uranium carbide heated in a hard glass bulb-tube; and then passed ammonia over the heated product. The dark green crystals melted to a black liquid which became solid as the reaction progressed. The product contained chlorine, and oxidized when ground in a mortar for retreatment. No definite compound was obtained. He recommended preparing the tritatetranitride by reducing uranium oxide with aluminium or magnesium in an atm. of nitrogen: $16Al+3U_3O_8+6N_2=3U_3N_4+8Al_2O_3$. If magnesium be employed, the magnesium nitride and oxide are readily removed by washing with dil. hydrochloric acid. Uranium nitride is a stable compound which, when heated in air, furnishes uranium oxide, U_3O_8. H. Herzer gave 10·044 to 10·088 for the sp. gr. at 25°/4°; and 76·4 to 76·7 for the mol. vol. It is not attacked by conc. hydrochloric or sulphuric acid, but oxidizing acids quickly decompose it. It is not changed by alkali-lye, but gives off ammonia when fused with potassium hydroxide. H. Moissan's preparation was decomposed by boiling alkali-lye. O. Heusler found that nitrogen reacts with heated uranium carbide in three stages, first forming **uranium pentitadinitride,** U_5N_2, thus: $5UC_2+N_2\rightleftharpoons U_5N_2+10C$; then **uranium pentitatetranitride,** U_5N_4, thus: $U_5N_2+N_2\rightleftharpoons U_5N_4$; and finally tritatetranitride: $3U_5N_4+4N_2\rightleftharpoons 5U_3N_4$. Both the pentitadinitride and the pentitatetranitride are soluble in dil. hydrochloric acid and all the nitrogen goes into soln. as ammonia. A. Remelé noted that uranium nitride exhibits a photoelectric effect.

H. N. Warren[30] reported a manganese nitride to be formed by passing ammonia over heated manganese oxide, but O. Prelinger was unable to confirm this. A. Guntz observed a trace among products obtained on heating manganese in nitrogen peroxide. W. C. Heræus found that manganese in an atm. of nitrogen at 1210°–1220° probably forms a nitride; and N. Tschischewsky heated 97 per cent. manganese in an atm. of ammonia and found that the metal absorbed the following percentage proportions of nitrogen at different temp.:

	330°	400°	500°	550°	600°	700°	800°	900°	1000°	1100°	1200°
N_2 .	0·16	0·58	2·63	9·22	14·39	14·36	4·35	10·59	7·20	4·00	1·73

and with ammonia in place of nitrogen,

	400°	500°	600°	700°	800°	900°	1000°	1100°	1200°	1300°
N_2 .	0·08	0·37	1·41	3·2	5·48	7·3	7·8	5·23	3·29	1·55

The results are plotted in Fig. 15. G. Tammann observed a reaction at 700° between nitrogen and manganese. E. Wedekind and T. Veit obtained **manganese heptitadinitride,** Mn_7N_2, by the action of ammonia on manganese heated by the oxyhydrogen flame, and found it to have stronger magnetic properties than the dipentita- or ditrita-nitrides. It is readily attacked by acids and alkalies. O. Prelinger showed that when powdered manganese oxidizes in air, some nitride is formed, and that when finely divided manganese, obtained by heating the amalgam, is heated in an atm. of nitrogen, or when the mercury is driven from manganese-amalgam in an atm. of nitrogen, **manganese pentitadinitride,** Mn_5N_2, is formed. F. Haber and G. van Oordt said that this nitride, so formed, is a mixture of manganese oxide and the ditritanitride.

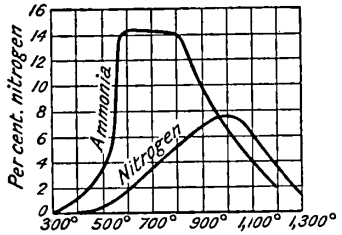


Fig. 15.—The Effect of Ammonia and Nitrogen on Manganese at Different Temperatures.

According to O. Prelinger, the dipentitanitride has a dull, metallic lustre, and, when finely divided, is somewhat darker than powdered manganese. On heating in a stream of hydrogen, ammonia is formed, whilst if hydrogen sulphide is substituted for the element, ammonium sulphide results. On treatment with ammonium chloride soln., ammonia, hydrogen, and the double chloride of manganese and ammonium are obtained: $Mn_5N_2+20NH_4Cl=12NH_3+2H_2+5(NH_4)_2MnCl_4$, and on fusion with caustic alkali much ammonia is liberated. When this nitride is heated in ammonia, it forms **manganese tritadinitride,** Mn_3N_2; and the same compound is formed if ammonia be substituted for nitrogen in the preparation of the preceding compound. H. Hardtung employed this process working at 760°–850° for 2–3 hrs. F. Haber and G. van Oordt, however, consider that this is the product of heating manganese-amalgam in nitrogen. G. G. Henderson and J. C. Galletly prepared this nitride by the action of ammonia on finely powdered iron at 800°. F. Fischer and co-workers made manganese nitride by the method indicated in connection with Fig. 11. According to O. Prelinger, the colour of the ditritanitride is the darker; it easily acquires a lustre under press.; its sp. gr. is 6·21 at 18°/4°. H. Hardtung gave 1000° for the temp. of formation, and 1100° for the temp. of decomposition. H. Herzer gave 550° for the temp. of decomposition. O. Prelinger said that manganese nitride behaves like the dipentitanitride towards hydrogen, hydrogen sulphide, and potassium hydroxide. I. I. Shukoff gave 18·18 to 22·62 mhos for the electrical conductivity of the powdered nitride. F. Haber and G. van Oordt studied the production of ammonia by the action of *hydrogen* on manganese nitride at 530°; and H. Hardtung, between 400° and 960°. A temp. of 850° was found to be most suitable. According to O. Prelinger, nitric acid dissolves manganese nitride only when hot; hydrochloric acid acts on it only in the presence of platinum; aqua regia dissolves it slowly; sulphuric acid acts only when hot, and with the conc. acid, sulphur dioxide is formed; acetic acid has no action; water slowly forms ammonia; potash-lye acts slowly in the cold, rapidly when heated, giving off ammonia; and when heated in nitrogen, the dipentitanitride is formed. H. Hardtung observed no evidence of the formation of cyanides by the action of carbon monoxide or dioxide on manganese nitride. E. Wedekind found that neither the dipentitanitride nor the ditritanitride shows any ferromagnetism when heated; but when cold the diheptitanitride is most magnetic, and the ditritanitride, least. O. Prelinger considers that manganese is quinquevalent in the dipentitanitride, and tervalent in the ditritanitride. I. I. Shukoff regarded the manganese nitrides as solid soln.

In 1808, A. B. Berthollet[31] found that when dry ammonia is passed over iron wire at a red-heat, the gas is decomposed into its elements, and the iron becomes very brittle, though it does not perceptibly increase in weight; L. J. Thénard said that the increase does not amount to 0·2 per cent.; and F. Savart added that after a 2 hrs.' passage of the gas, the iron appeared brittle; it exhibited the fine-grained fracture of steel and could be hardened like steel; but after 9 hrs.' passage, the metal was softer than common iron and no longer admitted of being hardened; the sp. gr. fell from 7·788 to 7·6637. C. Despretz, however, said that if ammonia, freed from moisture and carbon dioxide, be passed 6–8 hrs. over red-hot iron there is an increase in weight amounting to 7–11·5 parts per 100 parts of iron, and iron nitride is formed. This result was confirmed by H. Buff, F. Gröbe, A. H. Allen, G. J. Fowler, A. Rossel, G. T. Beilby and G. G. Henderson, A. H. White and L. Kirschbraun, E. B. Maxted, and G. Charpy and S. Bonnert.

An iron nitride occurs in nature. O. Silvestri found it as a very thin coating on the lava from the volcanic eruption at Mount Etna in 1874. The non-crystalline powder was silvery white; its sp. gr. was 3·147; it was slowly attacked by acids; and it had a composition corresponding with Fe_5N_2—some free iron was probably present. O. Silvestri called the mineral *siderazote;* and A. d'Achiardi, *silvestrite*—after its discoverer.

Nitrogen is slightly soluble in iron, and E. Jurisch showed that its solubility is proportional to the square root of the press. At 760 mm. press., 100 grms. of reduced iron absorbed

	878°	930°	981°	1033°	1084°	1136°
Mgrms. N_2. . . .	1·58	21·65	21·03	20·22	19·73	18·85

Absorption commenced at about 850°. A. Sieverts and W. Krumbhaar also showed that iron and steel absorb small quantities of the gas above 1200°. A. Sieverts found that when the reduced metal is continuously heated in the gas, a small amount is absorbed, and a little absorption was found to occur at ordinary temp. by A. W. F. Rogstadius, and F. Briegleb and A. Geuther. I. I. Shukoff detected no absorption of nitrogen by iron at 1250°. H. Braune found 0·02–0·062 per cent. of nitrogen in various samples of iron and steel. Grey pig iron had 0·002–0·020 per cent.; basic bessemer white pig iron, 0·020–0·030; basic open-hearth white pig iron, 0·025–0·035; forge white pig iron, 0·030–0·035; puddle bar for wire, 0·025–0·030; Swedish hearth iron, 0·006–0·008; basic open hearth steel, 0–0·030; acid bessemer steel up to 0·060. These numbers are probably all too high. This subject has been also discussed by B. Strauss, K. Iwase, A. Bramley, E. H. Schulz and R. Frerich, J. Petrén and A. Grabe, etc. According to J. H. Andrews, and A. W. F. Rogstadius, the absorption occurred when the metal is melted in the gas at a high press.; the former worked at 1000 atm. As indicated below, there is no evidence of the formation of a nitride by the direct union of the two elements, although many metallurgists—*e.g.* H. Braune, A. Pourcel, J. H. Andrews, and N. Tschischewsky—say that the absorbed nitrogen does form a nitride—if so, probably in the cooling metal, owing to the influence of other elements, and the action may be related to that which occurs during the formation of cyanides in the furnace. H. Wolfram found that pyrophoric α-iron begins to absorb nitrogen at 100°; and pure iron can retain 0·033 per cent. of nitrogen at its sintering temp. He found the following percentage proportions respectively in untreated iron and in iron after heating it in an atm. of ammonia: Purified iron, 0·0 and 0·033; skiegeleisen, 0·025 and 0·059; 80 per cent. ferromanganese, 0·039 and 0·46; manganese by the thermite process, 0·01 and 5·3; grey iron, 0·033 and 0·054; white iron, 0·011 and 0·017; steel, 0·022 and 0·03; phosphoriferous iron, 0·023 and 0·028; iron carbide, 0·035 and 0·045; ferronickel, 0·029 and 0·055; and ferrotungsten, 0·019 and 0·023. Hence, the presence of manganese particularly favours the absorption of nitrogen. According to E. Tilche, in the production of iron nitride and its subsequent conversion into ammonia by treatment with hydrogen, the gases are exposed to the action of a radioactive material, and the iron raised to a high electric potential and heated to redness during its treatment with nitrogen. I. Musatti and M. Croce studied the action of nitrogen during the cementation of steel. H. Braune said that the nitrogen in iron is exclusively combined with the ferrite, and not with the carbides; in ferrite the iron nitride is in solid soln. lowering the m.p., and the degree of solubility of the carbides. The absorbed nitrogen affects very materially the mechanical properties of the metal. Thus, J. H. Andrews found that 0·3 per cent. of nitrogen entirely suppresses the critical changes which occur in pure iron; and 0·25 per cent. of nitrogen and 0·6 per cent. of carbon lower the Ar_2-point, thus preserving the iron in the γ-form. N. Tschischewsky examined the effect of carbon, manganese, silicon, and aluminium on nitrogenous iron. H. Braune said that nitrogen increased the tensile strength of iron, and decreased the elongation; thus a steel with 1·15 per cent. of carbon had no elongation, and became entirely brittle with 0·030–0·035 per cent. of nitrogen. The results of some of N. Tschischewsky's experiments on the elastic limit and elongation of iron wires containing nitrogen are shown in Fig. 16. More nitrogen is required to make the elongation vanish, with steel containing less carbon. The hardness increases as the proportion of nitrogen increases; a rod of soft iron which had been heated to 800° in ammonia became so hard that it could be used as a drill; and a tube of malleable iron became so brittle that it could be broken by a blow from a hammer. H. Braune said that every 0·01 per cent. of nitrogen increases the electrical resistance of iron 3·23 per cent.; and it acts on the magnetic properties like additional carbon. The subject has also been discussed by H. le Chatelier, G. T. Beilby and G. G. Henderson, F. W. Harbord and T. Twynam, W. Giesen, C. E. Stromeyer, A. A. Blue, E. A. Sjösted, H. Herwig, P. Klinger, A. Fry, H. Tholander, L. Jordan and F. E. Swindells, A. Grabe, J. E. Johnson, L. E. Barton, W. E. Ruder and G. R. Brophy, G. F. Comstock and W. E. Ruder, A. E. White and J. S. Vaniek, and C. B. Sawyer. The relation of nitrogen and ammonia to the corrodibility of iron and steel has been discussed by O. A. Knight and H. B. Northrup, and H. E. Wheeler.

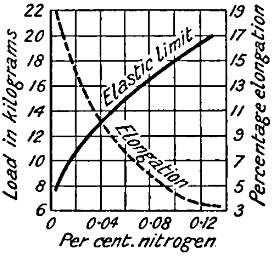


FIG. 16.—Elastic Limit and Elongation of Nitrogenous Iron.

In order to prepare the nitride, the iron should be in a finely divided condition, and a rapid current of ammonia, free from moisture and oxygen, should be employed. G. Tammann studied the reaction between nitrogen and iron. The most favourable temp. is 450°–475°. The nitride formed by the action of ammonia on iron has about 11 per cent. of combined nitrogen. This agrees with **iron heminitride,** Fe_2N, or Fe_4N_2. E. Frémy, and H. Herzer regard it as **iron pentitadinitride,** Fe_5N_2. The nitride is decomposed at 650°–670°. H. Hardtung found 450°–475° to be the most suitable temp. for the production of iron nitride. On the other hand, P. Herrmann said that at 1200° iron heminitride is formed quantitatively and readily. N. Tschischewsky found that with samples of iron, the maximum amount of nitride formed with purified iron is at 450°, Fig. 17, while pig iron and soft iron are sat. at about 600°. The higher proportion with sat. pig iron is not attributed to the action of carbon, but rather to "the finer state of the material." The retention of nitrogen by iron and steel is due to the presence of other impurities—*e.g.*, silicon, titanium, etc. The heminitride was made by E. Frémy, H. N. Warren, F. Girardet, and G. J. Fowler by heating ferrous chloride or bromide in ammonia. H. Hanemann used electrolytic iron foil; A. H. White and L. Kirschbraun, spongy iron; and G. J. Fowler, iron-amalgam. E. Frémy, and F. Briegleb and A. Geuther reported that at a dull red-heat iron can unite directly with nitrogen, but C. Stahlschmidt, and E. Baur and G. L. Voerman were unable to confirm this by working at ordinary press.; G. J. Fowler, by working with the iron and nitrogen in a sealed tube; and E. B. Maxted, by working at 2000 atm. press. D. Wolk, however, did say that if a mixture of barium and iron amalgams be quickly heated to 1000° in an atm. of nitrogen some iron nitride is formed. This statement, however, has not been confirmed.

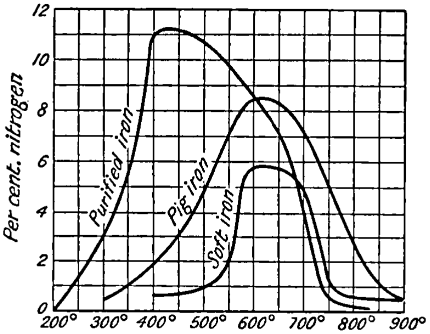


FIG. 17.—Effect of Ammonia on Iron at Different Temperatures.

The heminitride is completely decomposed above 600° when heated in nitrogen, below 600°, it possibly forms a more stable *iron tetritanitride*, Fe_4N. According to A. Fry, iron heminitride begins to break down at 440°, and on heating above that temp., it forms iron tetritanitride containing 5·9 per cent. of nitrogen. If the tetritanitride be heated to 560°, and cooled to 480°, it becomes magnetic. On heating to 630° magnetism again occurs, and is stronger the longer the heating period. The substance formed by the breaking up of the solid soln. with 0·5 per cent. nitrogen at 630°, undergoes a magnetic transformation at 740°. A. Fry represented his results by Fig. 18, where the region above *ABC* represents γ-iron; the lines *AFB* and *AEG* respectively denote the beginning and end of the separation of the solid soln. rich in iron; *GBH* represents the eutectic line with the separation of nitride-II (solid soln.-nitride needles); *DEF*, the magnetic transformation of nitrogenous ferrite; and *LM*, the magnetic transformation of the bodies produced by the decomposition of nitride-II. According to A. A. Noyes and L. B. Smith, if the equilibrium constant of the general reaction $2Fe_nN+3H_2=2Fe_n+2NH_3$ be expressed by K_1, and that of the reaction $N_2+3H_2=2NH_3$ by K_2, the dissociation press. of iron nitride can be expressed by K_1/K_2. The value of K_2 at 460°, calculated from known data, is $5{\cdot}10\times10^{-5}$. If the ratio Fe:N in the solid phase be greater than 9, the equilibrium constant $K_1=(P_{NH_3})^2/(P_{H_2})^3$ remains at 0·8–1·2, indicating probably the existence of a stable nitride, Fe_8N. When the Fe : N ratio becomes 7·7, the constant becomes 5·2 and increases to 30 with Fe : N=4·9 : 1; finally with Fe : N=2·6 : 1, the value of K_1 falls again to 2·1. These stages may correspond with the formation of metastable nitrides such as Fe_4N in solid soln. with the first, Fe_8N, or of two metastable nitrides such as Fe_6N and Fe_4N as separate solid phases; and finally of a stable nitride, probably Fe_2N. The dissociation press. of the nitrides in the above solid phases were calculated from K_1/K_2, and were found to be 20,000, 102,000, 590,000, and 41,000 atm. respectively. If, in the above reaction, complete equilibrium were established, all but about 0·1 per cent. of the ammonia would be dissociated, and the iron nitride, with its high dissociation press., would not form at all.

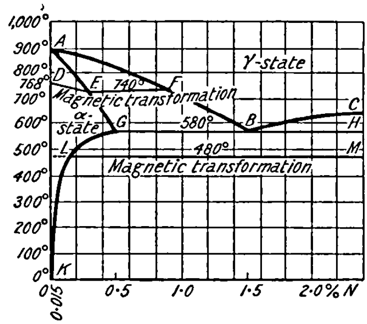
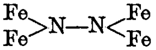


FIG. 18.—The System Iron-Nitrogen.

On heating iron in a current of ammonia at 680°, the tritacarbide, Fe_3C, present loses its total carbon and changes into the heminitride, Fe_2N. Two nitride layers are formed, the outer one, after quenching, contains over 8 per cent. nitrogen and consists of mixed crystals of heminitride, and the inner one consists of mixed crystals of the tritanitride. In the case of ordinary iron, these layers, though very hard, are too brittle to be of practical use. If, however, an alloy-steel with cobalt, vanadium, chromium, aluminium, titanium, or of chromium with one other element, is heated in ammonia at about 500°, more nitrogen goes into solid soln. than is the case with pure iron, and a very hard crust is obtained which does not flake off. The depth of the nitride layer is about 0·7 mm. The hardness cannot be increased by quenching, and is not reduced by slow heating to 440°. Above 560°, the nitride begins to decompose, and this is accompanied by a corresponding decrease of hardness. It is thought probable that from its mode of preparation, some unchanged iron would be present. The normal **ferrous nitride,** or **iron tritadinitride,** Fe_3N_2, was made by A. Guntz, by the action of lithium nitride on potassium chloroferrite; by using potassium chloroferrate, he obtained black-coloured **ferric nitride,** FeN. Iron tritadinitride may be pentitadinitride. F. W. Bergstrom prepared impure ferrous nitride by the action of ferrous tetramminothiocyanate on potassamide; and also by treating ferrous bromide with potassamide and then with a soln. of ammonium thiocyanate in liquid ammonia.

Iron heminitride is a dull grey powder which easily dissolves in dil. hydrochloric or sulphuric acid, forming ammonium and ferrous salts, and hydrogen. E. B. Maxted's arguments in favour of the view that the composition is Fe_3N_2 not Fe_4N_2(or Fe_2N), and that the so-called heminitride is a solid soln. of iron and the ditritanitride, $Fe_3N_2+Fe\rightleftharpoons Fe_4N_2$, as advocated by A. H. White and L. Kirschbraun, are: (i) nitrides with more nitrogen than is required for the latter formulæ are easily made; (ii) the mode of formation does not ensure the conversion of all the iron into nitride; (iii) the analogy with other nitrides; (iv) the existence of A. Guntz's Fe_3N_2, that is, Fe : N.Fe.N : Fe; and the transformation into ferrous and ammonium chlorides by the action of acids: $Fe_3N_2+Fe+10HCl=H_2+4FeCl_2+2NH_4Cl$; and $Fe_4N_2+10HCl=H_2+4FeCl_2+2NH_4Cl$. The mol. wt. of this nitride is unknown. The contained iron is therefore assumed to be in the bivalent state, and the nitrogen tervalent. The graphic formula, given by G. J. Fowler and P. J. Hartog, is:



$$\begin{matrix}Fe\\Fe\end{matrix}\!>N-N<\!\begin{matrix}Fe\\Fe\end{matrix}$$

G. J. Fowler gave 6·25 for the sp. gr.—C. Despretz's old value is 5·0. H. Herzer gave 6·985 to 6·992 for the sp. gr. at 25°/4°; and 44·0 for the mol. vol. G. J. Fowler and P. J. Hartog found the heat of soln. in dil. sulphuric acid to be 81·56 Cals., and the heat of formation, $2Fe+N_{gas}=Fe_2N+3\cdot4$ Cals. G. Charpy and S. Bonnerot showed that the nitride begins to decompose when heated to 500° in vacuo or in a current of nitrogen; and decomposition is rapid about 600°. This decomposition occurs under 18 atm. press., so that no formation of nitride is possible in nitrogen at these temp. H. Herzer gave 500° for the temp. of decomposition. E. Baur and G. L. Voerman found that when heated, the nitride decomposes into its constituents; at 350°, the dissociation is not perceptible; at 500°, the dissociation is very marked, and since at 600°, and 14 atm. press., no union of iron and nitrogen occurs, the maximum press. is greater than 14 atm. The reaction $2Fe_2N+3H_2\rightleftharpoons4Fe+2NH_3$ is reversible, and the equilibrium constant, $K=p^2/p_1{}^3$, where p denotes the partial press. of ammonia, and p_1 that of hydrogen. At 480° ± 3°, $K=6\cdot8\times10^{-4}$, and the dissociation press. is of the order 10^4 atm. As in the case of chromium nitride, the dissociation does not proceed until a definite dissociation press. has been attained, and then cease, rather does this press. exhibit a slow and continuous increase. This is taken to mean that iron and iron nitride do not form two constant phases, but rather one continuous phase. A. A. Noyes and L. B. Smith represent the system as one involving the reactions (i) $2Fe_xN+3H_2\rightleftharpoons2xFe+2NH_3$, where $(p_{H_2})^3K_1=(p_{NH_3})^2$; (ii) $N_2+3H_2\rightleftharpoons2NH_3$, where $pN_2(P_{H_2})^2K_2=(P_{NH_3})^2$, and it is known that $RT\log K_2=21400-11\cdot0T\log T+0\cdot00235T^2+22\cdot0T$, and for 460°, $T=460+273$, and $K_2=5\cdot10\times10^{-5}$; (iii) $2Fe_xN\rightleftharpoons2xFe+N_2$, where $P_{N_2}=f$ (solid phase). If all the reactions are in equilibrium, $P_{N_2}=K_1/K_2$. The equilibrium constant K_1 at 460° was found to vary with the proportion of nitrogen in the solid phase so that for

Ratio Fe : N . . .	17 : 1—9 : 1	7·7 : 1	4·9 : 1	2·6 : 1
K_1	1·0	5·2	30·0	2·1
Dissoc. press. P_{N_2} . .	20,000	102,000	590,000	41,000

These values of K_1 are taken to mean that there is first a formation of a nitride of small nitrogen content, say Fe_8N; then, either a metastable nitride as Fe_4N in solid soln. with the first one, or of two separate metastable nitrides as Fe_6N and Fe_4N as separate solid phases; and finally, of a stable nitride, say Fe_2N. By combining K_1 with K_2, the dissociation press. P_{N_2} were calculated. According to E. B. Maxted, iron nitride is only weakly magnetic; and the effect of various proportions of nitrogen on the magnetic properties of iron are illustrated by the curves, Fig. 18, showing the relation between the magnetic induction, B, and the magnetizing force, H; and Fig. 18, showing the relation between the permeability, μ, and the magnetizing force, H. E. Gumlich found the permeability of iron of the highest degree of purity to be 14,600 C.G.S. units.

E. Baur and G. L. Voerman studied the action of *hydrogen—vide supra*. According to G. J. Fowler, in *air* or *oxygen*, there is a very slight action at 120°; and oxidation is visible at 200°—brown ferric oxide is formed, but no nitrogen is oxidized; *water* vapour, at 1000°, produces a slow evolution of ammonia. A. Rossel prepared a nitride, which is readily decomposed by water, by heating a mixture of finely powdered calcium carbide and powdered iron while exposed to air. G. J. Fowler showed that very little if any nitrogen is oxidized during the simultaneous action of acids and *hydrogen dioxide.* The nitride takes fire spontaneously, or else on warming, when placed in *chlorine* gas—ferric chloride and nitrogen, but not nitrogen chloride, were formed—with chromate-water, iron and ammonium chlorides are formed. The attack of *bromine* is slow, even on warming, and ammonium bromide is formed. An ethereal soln. of *iodine* does not attack the nitride. Cold *hydrogen chloride* does not attack the nitride; chemical action begins about 220°, and is rapid at 350°, forming ferrous and ammonium chlorides. Dil. *hydrochloric and sulphuric acids,* as indicated above, dissolve the nitride, forming ferrous and ammonium chlorides. The attack by *hydrogen sulphide* begins about 200°: $2Fe_2N+6H_2S=4FeS+2NH_4HS+H_2$. The nitride is attacked by conc. *nitric acid* slowly—ammonium nitrate and nitrous and nitric oxides are formed. Oxidation of *nitric oxide* began about 120° and became rapid at 170°, and nitrogen is formed: $Fe_2N+2NO=2FeO+N_2$. No sign of the formation of cyanides was observed by heating a mixture of iron nitride and *carbon,* but if sodium be present, sodium cyanide is produced. There is a slight reaction with *carbon monoxide* at a red-heat, but no cyanogen was evolved; with *carbon dioxide* at 448°–538° some nitride is oxidized. No appreciable change occurred when iron nitride and *phenol* were heated in a sealed tube at 220°; and with *ethyl iodide,* no action was observed below 150°; and, at 200°–230°, the reaction appeared to be: $2Fe_2N+10C_2H_5I=2NH_4I+10C_2H_4+4FeI_2+H_2$. A neutral soln. of *copper sulphate* has no action on iron nitride, but if the soln. be slightly acidified, copper is precipitated and ammonium sulphate is formed.

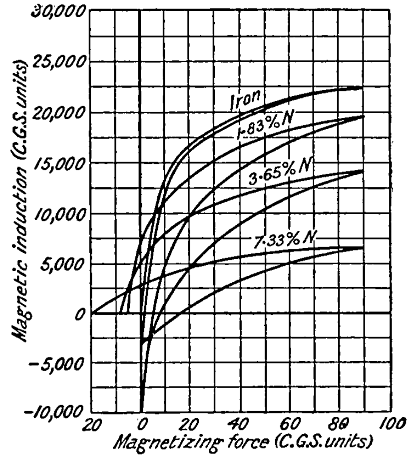


FIG. 19.—Relation between Magnetizing Force and Induction.

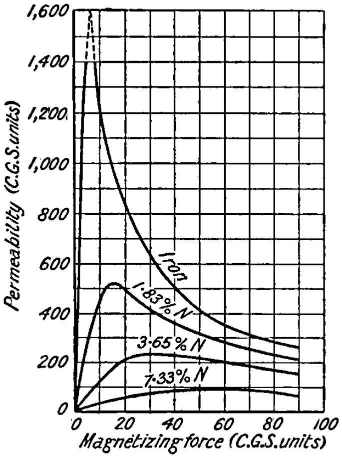


FIG. 20.—Relation between Magnetizing Force and Permeability.

E. Frémy[32] observed that **cobalt nitride** is not formed when cobalt sesquioxide or cobalt chloride is heated in ammonia gas; G. Tammann observed no reaction between nitrogen and cobalt at 700°. According to F. Vorster, the small observed increase in weight which occurs when powdered cobalt is heated in ammonia is really due to oxidation owing to the presence of traces of air. The cobalt, however, decomposes the ammonia into its elements; cobaltic hydroxide is not changed by ammonia gas at 170°; and an alcoholic or aq. soln. of ammonia in a sealed tube with cobalt sesquioxide produces no change. H. N. Warren said that when cobalt oxide or chloride is heated in ammonia gas, a nitride is formed. W. R. Hodgkinson and C. C. Trench heated cobalt sulphate in ammonia gas and observed the formation of an oxide and sulphide, but no nitride. E. St. Edme said that when cobalt is maintained at a red-heat for a considerable time in an atm. of nitrogen, the metal becomes passive towards nitric acid, presumably owing to the formation of a superficial film of cobalt nitride. A. Sieverts said that cobalt and nitrogen do not form a nitride at a temp. over 1150°. G. T. Beilby and G. G. Henderson heated cobalt in a current of ammonia, and starting the action at 470° and subsequently lowering the temp., they obtained a product with 10·33 per cent. of nitrogen. A. C. Vournasos allowed a mixture of cobalt cyanide and oxide to fall in small quantities at a time through an electric arc between carbon poles in an atm. of nitrogen. The brown product corresponded with **cobalt tritadinitride,** Co_3N_2. F. W. Bergström obtained cobaltous nitride, Co_3N_2, as a black solid, by heating cobaltous amide to 120°. It is almost unaffected by water. P. Herrmann said that powdered cobalt at 1300°, does not form a compound with either nitrogen or ammonia, but there is a marked volatilization of the metal. The metal in ammonia at 300° increases in weight, and when kept a long time at 250°, **cobalt tritanitride,** Co_3N, appears to be formed in very small amounts.

W. R. Grove obtained a product, thought to be **nickel nitride,** by the method he employed for zinc nitride. G. Tammann observed no reaction between nitrogen and cobalt at 700°. F. Vorster found that at 200°, nickel sesquioxide is reduced to nickel monoxide, and at a higher temp. to nickel; nickel hydroxide is not attacked by ammonia at 170°; and in a sealed tube at 150°, aq. ammonia slowly reduces nickel sesquioxide to nickel monoxide with the probable formation of nitric acid. In no case was nickel nitride produced. H. N. Warren believed he had produced nickel nitride by a process analogous to that used for cobalt nitride. P. Herrmann found that nickel chloride is reduced by ammonia at 500°, forming nickel. Finely divided nickel at 1400° does not react with either nitrogen or ammonia, but some metal is volatilized. At 50°, nickel powder absorbs some ammonia gas. When powdered nickel, or nickel chloride, is heated in a sealed tube with aq. ammonia, nickel hydroxide is formed, and in the absence of water, the nickel powder remains unchanged. P. Herrmann, and A. Smits obtained a black mass, probably nickel nitride, by heating dry nickelous chloride with magnesium nitride. G. T. Beilby and G. G. Henderson heated nickel in a current of ammonia at 500°, and obtained a product with 7·5 per cent. of nitrogen. A. C. Vournasos prepared **nickel tritadinitride,** Ni_3N_2, by a process similar to that used for the corresponding cobalt nitride. G. S. Bohart prepared the tritadinitride by heating nickelamide in vacuo at 120°. Nickel tritadinitride is a dull black powder which, under the microscope, consists of minute, roughly spherical particles. With steam at a red-heat, ammonia is evolved; and ammonia and hydrogen are evolved when the nitride is heated to redness in hydrogen. A. C. Vournasos said that the nitride burns in oxygen to nickel peroxide. It is soluble in dil. hydrochloric or sulphuric acid, forming nickel and ammonium salts. According to F. Wolfers, nickel is attacked by nitrogen at about 300°, producing a volatile nitride which is unstable at 600°. The volatile nitride is said to attack platinum.

F. Fischer and F. Schröter [33] said that the platinum metals do not form nitrides. G. T. Beilby and G. G. Henderson observed that while heating platinum in ammonia produced no **platinum nitride,** a profound change in the physical structure of the metal occurred; and G. G. Henderson and J. C. Galletly obtained a similar result with respect to **palladium nitride.** L. Arons believed that he obtained a fine sublimate of nitride when an arc is made between platinum electrodes in nitrogen. S. M. Jörgensen, and H. Wolffram obtained an explosive black powder, thought to be platinum nitride, by heating platinum ethylamminochlorides. L. Tschugaeff obtained indications of the formation of a platinum nitride in the reduction of potassium chloroplatinite with tertiary amines.

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§ 13. The History of Ammonia

In the *Historia* of Herodotus (**4**. 181), written in the fifth century before our era, it is said that "there are pieces of salt in large lumps on the hills" of Libya, and the Ammonians, who lived there, "have a temple resembling that of Theban Jupiter." The first-century writers, Strabo, in his *Geographica* (**1**. 3, 4), and Dioscorides, in his *De medicinali materia* (**5**. 126), allude to this salt; while Pliny, in his *Historiæ naturalis* (**31**. 41, *c*. 77), referred to a variety of salt called *hammoniacum*—from *ἄμμος*—in allusion to its occurring in the sands; he also referred to the calcination of *nitrum* producing a "vehement odour." This shows that a number of salts were confused under one term (**2**. 20, 1). G. Apicius, in his *De re culinaria*, also written in the first century of our era, mentioned the use of *sal ammoniacum* in cooking; and a similar term was employed in the second century by Arrian, in his *Ἐγχειρίδιον*; in the fifth century by Simplicius, in his commentary on Arrian's *Enchiridion;* and about the same time by Ætius in his *Medicæ artis principes*. Dioscorides pointed out that *ἀμμωνιάκον* possessed a fibrous structure which enabled it to be readily divided, and to be thus easily distinguished from common salt. Nevertheless, in all these cases, H. Kopp[1] was able to say that *sal ammoniacum* was considered to be the same as rock-salt. The Latin translations of some of the Arabic writers of the eleventh and twelfth centuries—*e.g.* Albucases' or Alzaharavius' *Servitor;* Avicenna's *Fractatulus alchemiæ;* and Geber's *De investigione magisterii*—applied the term *sel ammoniacum* to what is now known as sal ammoniac. Basil Valentine speaks of sal ammoniac, Armenian salt, salt from Armenia, and Armenian sal ammoniac; and from the sixteenth century onwards, writers—A. Cæsalpinus, J. R. Glauber, G. Agricola, A. Libavius, F. Sylvius de la Boë, N. Lemery, etc.—used the term *sal ammoniacum* or *sal armeniacum* for ammonium chloride as distinct from sodium chloride, or for salts containing volatile alkali as distinct from those containing fixed alkali; and towards the end of the seventeenth century the term *sal ammoniac* was in almost general use for ammonium chloride. H. Kopp said that sal ammoniac was probably first brought to Europe from Asia Minor, where it occurred naturally, and was hence called *Armenian salt.* A. Cæsalpinus said that it was made *ex urina chamelorum.* The preparation was described in Geber's *De investigatione magisterii* somewhat as follows:

> Sal ammoniac is made from two parts of human urine, one part of the sweat (sudoris) of the same, one part of common salt, and one and a half parts of the soot of logs or sticks. When these have been heated together until the moisture is evaporated, true and useful sal ammoniac is sublimed. Mix the product with common salt and sublimate again, when the preparation is complete.

This mode of preparation reappeared in various forms in the works of later writers —*e.g.* N. Lemery, and A. Libavius. R. Boyle said:

> Though sal-ammoniac that is made in the East may consist in great part of camel's urine, yet, that which is made in Europe, and is commonly sold in our shops, is made from men's urine. . . . Sal-ammoniac might be made much cheaper if, instead of fetching it beyond the sea, our country-men made it at home; which it may easily be, and I am ready to give you the receipt, which is no great secret.

In 1716, C. Sicard, and in 1751, F. Hasselquist described the Egyptian method of making sal ammoniac; in 1719, L. Lemery showed how the salt was obtained directly from the soot collected in burning camel's dung; and in 1736, H. L. Duhamel du Monceau found that salt is not necessary in Geber's recipe, and that the soot is a purifying agent. In 1583, L. Thurneysser reported that sal ammoniac was made in Europe earlier than 834 A.D., but H. Kopp said that this report is given *mit seiner gewöhnlichen Lügenhäftigkeit.* Sal ammoniac was manufactured at Edinburgh in 1756, at Brunswick in 1759, and at Paris in 1770.

In the Latin translation of Geber's *Testamentum* there is a note: *De salibus animalium, piscium, volatilium, vegetabilium, et aliorium,* from which it appears to be highly probable that he obtained volatile alkali or liquor ammonia by heating some of these products, but he recorded no specific observations on this subject. In the fourteenth century, Raymond Lully, the assumed author of *Experimenta,* dated 1330, alluded definitely to aqua ammonia as *mercurius animalis* or *spiritus animalis,* for he said:

> Take in goodly quantity the early morning urine of boys from eight to twelve years of age. Place this in a glass alembic to completely putrefy. . . . See that the beak of the alembic is wide and open else the salt rising from the bottom of the alembic and sublimating will choke the neck of the beak. When they flow into the receiver, which if they do they will break the vessel, as happened in my case . . . you will clear out the salts with care and will keep them in a glass vessel well corked, for the salt is very volatile. . . . Beware of the fumes when opening the bottle, they are very pungent.

About the middle of the fourteenth century, Johann de Rupescissa, or Roquetaillade, referred to a substance which gave precipitates with metallic salt soln., and which was obtained by heating animal products in a closed vessel. Isaac Hollandus, a century later, called it *spiritus salis urinæ;* and this was followed by analogous allusions to this substance, by J. Mayow; A. Sala—*spiritus urinæ;* J. B. van Helmont—*spiritus salis lotii,* or *spiritis salis cruoris;* J. R. Glauber—*spiritus urinæ* or *spiritus volatilis salis armoniaci.* O. Tachen, R. Dossie, and A. Sala said that if *spiritus urinæ* (aq. ammonia) be mixed with *spiritus salis* (hydrochloric acid) the product is in all respects like ordinary sal ammoniac. This is considered to be the first direct synthesis of this salt (ammonium chloride). J. Kunckel inquired whence comes the causticity of the spirit of urine obtained when sal ammoniac is treated with quicklime, and considered that the causticity was carried from the lime to the volatile alkali during the treatment of the sal ammoniac. The term *spiritus urinæ* soon became *volatile salis ammoniaci;* and T. Bergman and others called it *ammoniacum.* Raymond Lully, R. Boyle, J. B. van Helmont, N. Lemery, F. Hoffmann, C. J. Geoffroy, J. Kunckel, etc., made various allusions to the properties of the substance obtained by heating sal ammoniac with acids, alkalies, or lime. Stephen Hales found that by heating of a mixture of sal ammoniac and lime in a retort, although he collected no gas, the water of the pneumatic trough was drawn backwards into the retort. In 1774, J. Priestley repeated the experiment, using mercury in his pneumatic trough, and thus definitely isolated ammonia gas which he named *alkaline air.* He said:

> It occurred to me that an alkaline air might be expelled from those substances containing volatile alkali. Accordingly, I procured some volatile spirit of sal ammoniac, and having put it into a thin phial, and heated it with the flame of a candle, I presently found that a great quantity of vapour was discharged from it; and being received in a vessel of quicksilver, it continued in the form of a transparent and permanent air, not at all congealed by cold.

For a time, it was thought that the volatile alkali, aqua ammonia, was a variety of fixed alkali, and that the latter could be converted into the former—*e.g.* L. C. Cadet de Gassicourt, and P. J. Macquer—but this hypothesis was no longer tenable after J. Priestley had isolated the gas, and shown that it could be decomposed by electric sparks so as to produce a combustible gas. In 1777, C. W. Scheele assumed that volatile alkali is a compound of nitrogen and phlogiston. In 1785, C. L. Berthollet found that when the gas is decomposed into its constituents by means of the electric spark, it furnishes approximately 0·725 vol. of hydrogen to 0·275 vol. of nitrogen, or 0·193 grm. of hydrogen to 0·807 grm. of nitrogen. More exact data were obtained by W. Austin, H. Davy, W. Henry, and A. B. Berthollet; but the general results confirmed the earlier observations of C. L. Berthollet. For ammonium, *vide* **4**, 31, 38.

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§ 14. The Occurrence of Ammonia

A. Fowler and C. C. L. Gregory[1] found that many lines in the ultra-violet spectra of the sun and of ammonia are the same, and it was therefore inferred that ammonia is present in the absorbing atmosphere of the sun. The occurrence of ammonia in atm. air, and in rain-water, snow, and hail has been discussed in connection with atm. air. While spring waters usually contain little or no ammonia, river-water and sea-water may have appreciable amounts. Thus, J. B. J. D. Boussingault reported 0·016 to 4·9 mgrms. of ammonia per litre of river-water; and W. Knop, 0·7 to 2·35 mgrms. J. B. J. D. Boussingault found 2·0 mgrms. of ammonia per litre in the canal at Dieppe; A. Audoynaud, 0·16 to 1·22 mgrms. off Palavas, near Montpellier; L. Dieulafait, 0·221 mgrm. from the Mediterranean Sea, 12 kilometres from Marseilles; 0·204 mgrm. off Ismaila, 0·136 mgrm., in the Bay of Bengal, 0·340 mgrm. off the Coast of Cochin China; 0·176 off Socatora, off Cape Gardafuy, and in the waters of the Red Sea; E. Marchand, 0·57 mgrm. in the canal at Fécamp; A. Vierthaler, 13·8 mgrms. in the waters of the Adriatic Sea at Spalato; and T. E. Thorpe and E. H. Morton, 1·1 mgrm. in the waters of the Irish Sea. Observations were also made by J. Bouis, G. Forchhammer, A. Houzeau, W. Knop, L. Studdert, and A. Terreil. According to L. Dieulafait, ammonia occurs in the sea-water of all latitudes; and the proportion does not increase with the evaporation of the water, since some escapes into the air. J. Murray reported ammonia in the mineral waters of Cheltenham and Gloucester; A. Chevallier, in those of Passy and Chaudes Aigues; A. J. Béchamp, in those of Vergèze; F. Parmentier, in the bituminous waters of Clermont, etc. The ammonia in river-waters is sometimes derived from sewage, the organic matter of which, in the course of its decomposition, forms amino-acids, and then ammonium compounds. Ammonia is readily oxidized by certain organisms, forming nitrites and nitrates. The presence of ammonia is therefore often regarded as an indication of pollution by nitrogenous matters—*e.g.* urine.

L. Dieulafait[2] found ammonia in the deposits obtained during the evaporation of sea-waters, and he detected it in gypsum beds, and it is disengaged in the manufacture of plaster of Paris from gypsum. He said that all saline waters obtain their mineral matter from salt-bearing formations which contain a considerable quantity of ammoniacal salts. The ammonia which accompanies the boric acid emitted from the lagoons in Tuscany is said to be derived from the saline beds in which the boric acid occurs, the part played by the volcanic agent being purely mechanical. There is 0·07 mgrm. of ammonia per litre in the water of Lake d'Enghien, while the sulphur spring, fed by the lake, contains 5·06 mgrms. per litre. This is explained by assuming that the water from the lake passes over sediments from which it dissolves ammonium salts. Hence, added L. Dieulafait, all saline mineral waters ought to contain ammonium salts, whether these waters be sulphurous or not, thermal or not. A. Vogel reported ammonia in the rock-salt of Hall, Rosenheim, Friedrichshall, Orb, Kissingen, and Dürkheim. L. Glaser observed ammonia in the vicinity of a coal-deposit which had burnt at Duttweiler. The presence of ammonia in the vapours of the boric acid fumaroles of Monte Cerboli, etc., was noted by C. Blondeau, C. Schmidt, O. Popp, and H. St. C. Deville and F. Wöhler. Ammonium chloride was found in the vicinity of Hecla, by R. Bunsen; about the fumaroles of the Valley of Ten Thousand Smokes, Alaska, by E. T. Allen and E. G. Zies; and in the vicinity of Vesuvius, by A. Scacchi, and A. Ranieri. The subject was discussed by L. Palmieri, H. St. C. Deville, C. G. B. Daubeny, A. Gautier, and W. S. von Waltershausen. According to J. Stoklasa, the ammonium salts found on the lower portions of the lava of Vesuvius are not due to the burning of vegetation, because he found ammonia in lava at an altitude of 900 metres in places where no vegetation is present; in the sand of the crater; and in the gases streaming out of the crater. A. del Campo found ammonium fluoride in a sublimate from Chinyero, Canary Islands—*vide* ammonium chloride (**2.** 20, 16).

Soils readily adsorb gases of various kinds, and the occurrence of ammonia in soils has been discussed by W. Knop,[3] A. Mayer, A. Müntz and H. Coudon, E. Marchal, and M. Berthelot and G. André. The ammonia is derived from the decomposition of nitrogenous matter in the soil. P. Ehrenberg has discussed *Der Kreislauf des Ammoniakstickstoffs in der Natur*. C. G. Gmelin observed that ammonia is given off when some minerals are calcined. J. Bouis noted that most clays contain some ammonia. The ammonia in clays and ferruginous ores is supposed to have been absorbed from the atm. and partly derived from the oxidation of iron in contact with air and moisture. M. Faraday showed that clay which has been heated to redness, absorbed an appreciable quantity of ammonia from the air during eight days' exposure. J. B. J. D. Boussingault found that ferric oxide from the middle of a deep boring near Marmato contained ammonia. The presence of ammonia in iron ores, dolomite, clay, soil, and other porous substances has been noted by L. N. Vauquelin, A. Chevallier, M. Faraday, J. Bouis, W. Knop, A. Mayer, L. Dieulafait, and W. Austin. The occurrence of ammonia in iron-rust was noted by C. Bourdelin in 1683, and later, by L. N. Vauquelin, M. E. Chevreul, and J. Reiset; and M. Barré, and P. Regnard detected an odour of ammonia on breaking several ingots of steel, prepared by a special process, and gas escaped accompanied by a slight hissing noise. Analyses showed that the gas is mainly hydrogen and hydrocarbons—no ammonia or nitrogen was detected.

F. Sylvius de le Boë [4] noted the occurrence of ammonia in the juices of some plants—*e.g.* the spoon-wort. A. Pleischl found that the juices of many plants contain ammonia. E. Schultz and H. Schultze found it in the juice of the maple, birch, vine, and sugar-beet; and J. von Liebig, in tobacco juices. N. Castoro found ammonia in the embryo of plants. A. Hosaeus found ammonia in peas, and indeed in all the parts of plants he investigated; but, added E. Reichardt, the stalks of swallow-wort, and of corn, are free from ammonia in spring. H. Pellet said that ammonia is stored in some plants in the form of ammonium magnesium phosphate. E. Formanek,[5] and W. Kühne reported that the expired air of animals usually contains traces of ammonia. T. Rumpf, E. Hallervorden, W. Heintz, C. Neubauer, and C. M. Tidy and W. B. Woordmann showed that the urine of birds and reptiles has a large proportion of acid ammonium urate; and the urine of mammals contains a small proportion this salt. The presence of ammonia in blood was discussed by M. Nencki and co-workers, O. Hammarsten, H. Winterberg, S. Salaskin and co-workers, M. Jacoby, G. Dujardin, R. Beaumetz and A. Hardy, etc.

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§ 15. The Preparation of Ammonia

The methods available for the preparation of ammonia can be conveniently arranged according to the source of the nitrogen: (i) from free nitrogen; (ii) by the reduction of nitrogen oxides; (iii) from ammonium salts; (iv) by the action of water on the nitrides, amides, etc.; (v) by the decomposition of organic nitrogenous compounds; and (vi) by bacterial action. A review of the German patents on the subject has been made by G. Schuchardt in his *Die technische Gewinnung von Stickstoff, Ammoniak und schwefelsaurem Ammonium* (Stuttgart, 1919).

1. *The formation of ammonia from elemental nitrogen.*—In 1807, H. Davy[1] reported that nitric acid and ammonia are formed during the electrolysis of distilled water with air in soln.—**1.** 3, 6. Lord Rayleigh could not confirm the formation of ammonia, and E. Tiede and A. Schleede failed to obtain a trace of ammonia under varying conditions, and under press. up to 150 atm. On the other hand, F. Fichter and R. Suter said that Lord Rayleigh's failure to verify H. Davy's observations was due to his use of platinum electrodes and a high current density in place of gold electrodes and a low current density. F. Fichter and R. Suter obtained 0·3 mgrm. of ammonia per 100 amp. per min. with nitrogen at 200 atm. press., an electrolyte of one per cent. sulphuric acid, and platinum electrodes of large surface and thickly platinized. The cathode surface quickly loses its efficiency and has to be renewed; its activity cannot be restored by oxidation. No formation of ammonia was observed when a mercury cathode was used. R. Nithack obtained a patent for utilizing the reaction.

C. Zenghelis obtained small yields of ammonia by passing mixtures of nitrogen and hydrogen (1 : 3 vol.) through water or acidulated water with colloidal metals—platinum, palladium, gold, silver, copper, or mercury—in suspension, and at 90°. Small yields were also obtained by passing nitrogen through a mixture of zinc and dil. sulphuric acid at 90°; nascent electrolytic hydrogen; and from a warm soln. of ammonium chloride and potassium nitrate with colloidal platinum as catalyst. H. G. Falk and R. H. McKee found that nitrogen, at 300 lbs. per sq. in. press., and in contact with water at ordinary temp., forms ammonium nitrite $N_2+2H_2O=NH_4NO_2$, as well as traces of nitrate derived from accidental traces of oxygen in the water. An increased yield of nitrite was obtained at 1800 lbs. press., and also with a mixture of alcohol and acetone in place of water as solvent. In vitreous silica or glass vessels, the reaction occurred only in the presence of a catalyst—say a clean piece of iron. J. J. van der Bossche hydrolyzed nitrogen by passing that gas under press. into a soln. which is being electrolyzed between electrodes of ferromanganese. C. B. Jacobs forced nitrogen through a porous cathode and obtained nitric oxide or nitrates during the electrolysis of alkaline soln. K. F. Bonhöffer, and A. L. Marshall and H. S. Taylor doubted if atomic hydrogen can combine with molecular nitrogen to form ammonia—*vide supra*, nitrogen. A. J. Prince showed that the reaction: $N_2+3H_2+2CO+2H_2O=2H.COONH_4$, said by P. R. de Lambilly to occur in the presence of a catalyst, does not occur with platinized asbestos. K. A. Hofmann and E. Will observed the formation of ammonia in the combustion of air in some hydrocarbons. H. Hampel and R. Steinau heat ammonium chloride in the presence of iron filings and the reaction $Fe+2NH_4Cl=FeCl_2+2NH_3+H_2$ occurs; if in the presence of dissociated nitrogen, the nascent hydrogen so formed reacts $3Fe+6NH_3+6HCl+2N=3FeCl_2+6NH_3+2NH_3$, giving 2 mols more ammonia than the ammonia started with. H. Davy noticed that water distilled in contact with a mixture of charcoal and potash furnishes ammonia which he was inclined to attribute to the hydrogenation of the adsorbed nitrogen.

According to C. Morren, A. Geitz, and A. Perrot, when an electric discharge is passed through a mixture of hydrogen and nitrogen, ammonia is formed: E. P. Perman said that if the press. of the mixed gases is increased from one to two atm., the yield of ammonia is doubled. A. Findlay observed the formation of ammonia when the mixed gases are exposed to the brush discharge; and, according to P. and A. Thénard, E. Warburg and W. Rump, C. Chabrier, and W. F. Donkin, a similar result is obtained if the mixed gases be exposed to the silent electric discharge. M. Berthelot obtained a conc. of about 3 per cent. of ammonia by the action of silent discharge on a mixture of hydrogen and nitrogen. E. Hiedemann passed a mixture of hydrogen and nitrogen through an electron tube with an ionization potential a few volts above that of both gases, and obtained a relatively high yield of ammonia; and L. Hamburger found that the conditions which favour the formation of active hydrogen or nitrogen give higher yields of ammonia. C. T. Kwei found that ammonia bands appear at 23 volts, but not at 17 volts. A. R. Olson attributed this to the presence of activated nitrogen at the higher voltage only as observed by T. R. Hogness and E. G. Lunn, H. Sponer, and H. H. Storck and A. R. Olson—*vide supra*, for the action of activated hydrogen or nitrogen.

A. Mirimanoff showed that the most favourable temp. for the formation of ammonia in the silent discharge lies between 450° and 550°; above 650°, no ammonia was formed owing to the increase in *l'instabilité* of ammonia at elevated temp. M. le Blanc and J. H. Davies inquired if the law of mass action applies for the silent electrical discharge. They found that when dry ammonia gas is exposed to the silent discharge at constant temp. and constant current, the rate of decomposition is nearly proportional to the press.; temp. has a comparatively small influence on the rate of decomposition; a rise of 100°, or an increase of the current by one-third, nearly doubles the rate of decomposition. The presence of an excess of hydrogen diminishes the rate of decomposition, whereas an excess of nitrogen increases it. The luminosity of the discharge is much increased by nitrogen, but not by hydrogen. The final condition of equilibrium attained is very little affected by the strength of current used. The ratio $[N_2][H_2]^3/[NH_3]^2$ for different mixtures of hydrogen and nitrogen is not even roughly constant. Hence, the law of mass action does not hold, being apparently valid only when the temp. is so high that the reactions occur under the influence of heat alone. H. B. Moses obtained a sudden chilling of the gases and a correspondingly high yield by forming an arc in a mixture of hydrogen and nitrogen in the vicinity of liquid nitrogen. A. Makowetzky studied the formation of ammonia in the glow discharge with cooled electrodes. A. Günther-Schulze observed no signs of the union of hydrogen and nitrogen in the glow discharge, rather is ammonia thereby completely decomposed.

H. St. C. Deville noted that appreciable quantities of ammonium chloride are produced if a mixture of hydrogen and nitrogen be sparked in the presence of hydrochloric acid; in fact, as H. B. Dixon showed, the conversion of the 3 : 1 mixture of hydrogen and nitrogen is complete if the ammonia be continuously removed from the system by an acid. E. Baur, E. Briner and co-workers, and A. de Hemptinne have also made observations on the synthesis of ammonia by exposing the mixed gases to the electric discharge. On the other hand, J. Priestley, C. L. Berthollet, A. B. Berthollet, W. Henry, and H. Buff and A. W. Hofmann observed that when a succession of electric sparks is passed through dry ammonia, decomposition occurs, and the vol. of gas is doubled. H. St. C. Deville said that there is always a trace of ammonia left after a protracted sparking of the gas. The reaction is, indeed, reversible. R. Pohl passed a silent discharge at 5000–10,000 volts through an ozonizing tube containing ammonia, and found that the presence of traces of moisture inhibits the decomposition of the gas to a considerable extent, and the efficiency also became less when the current was increased; increase of the e.m.f. employed, of the press. of the gas, or of the thickness of the layer traversed had, however, an opposite effect. A. Classen obtained ammonia by subjecting a mixture of hydrogen and nitrogen to the simultaneous action of the silent and spark electric discharges in presence of catalysts—*e.g.* metals and metallic alloys, supported on carriers of an acidic nature. Silica, prepared from water-glass, is well suited for this purpose, as it readily absorbs colloidal metals such as gold, platinum, metals of the platinum and iron groups, as well as their alloys. The efficiency of the catalyst is improved by the presence of a protective colloid—*e.g.* galatose. The mixed gases are passed over the catalyst between two electrodes, one being a good conductor, like copper, and the other a bad conductor, like glass or porcelain. The latter may be immersed in cold water and may concentrically surround the former, the contact material being in the intervening space. The temp. may range from 25° to 90°, according to the conditions, and the press. may be normal, or higher than normal.

E. B. Andersen studied the synthesis of ammonia by the action of a stream of slow-moving electrons on mixtures of the constituent elements. A current was passed between a glowing tungsten filament and two platinum electrodes in the mixed gases. The curves connecting the velocity of formation of ammonia with the applied e.m.f. show maxima at 22, 26, and 33 volts. No appreciable amount of ammonia was produced below an applied e.m.f. of 17·7 volts—the ionizing potential of nitrogen. Hence it is supposed that the first step in the production of ammonia is the ionization of the nitrogen mols. The maximum rate of formation did not correspond with the stochiometrical mixture. H. H. Storch and A. R. Olson found that an increased percentage of nitrogen favours a higher rate of reaction; the formation of ammonia cannot be detected unless an arc is present; and the rate of formation of ammonia depends primarily on the diameter of the hot filament. The variation in the rate of reaction at specific voltages is such as to give abrupt increases with e.m.f. about 4 volts apart. The wave-type of curve observed by E. B. Andersen is attributed to the superposition of a curve showing the effect of the accelerating voltage on the rate of reaction, and a fatigue effect in the mechanism used for absorbing the ammonia.

E. Briner and E. Mettler studied the maximum conc. of ammonia obtained by circulating a mixture of hydrogen and nitrogen through a tube containing a spark-gap; and E. B. Maxted examined the relative efficiency of various types of spark. The sparks from an induction coil were found to be very inefficient, and energetic ammonia formation was found to occur only when the electrodes were sufficiently close to transform the ordinary spark discharge into a small high-tension arc, accompanied by a visible and apparently continuous flame of high temp. With the 3 : 1 mixture of hydrogen and nitrogen flowing at the rate of 40 c.c. per hour, less than 0·1 per cent. of ammonia was contained in the issuing gas with a spark discharge having a 10 mm. spark-gap; with a 5 mm. spark-gap having an incipient flame, 0·25 per cent. of ammonia was formed; and with an arc flame with a spark-gap of 1·5 mm., 0·8 per cent. of ammonia, and when the gap was 0·5 mm., 1·1 per cent. of ammonia was present. E. P. Perman suggested that the formation of ammonia by the electric discharge is due to the formation of ions; but E. Briner and A. Baerfuss said that the discharge dissociates the mols. of nitrogen and hydrogen into atoms, which, diffusing into a zone of lower temp., unite to form ammonia. In support of this hypothesis they stated that by reducing the press. to 100 mm., and also by increasing the nitrogen content of the mixture sparked, the yield of ammonia was augmented. Thus, E. Briner and J. Kahn found:

Initial press. . . .	696·15	463·15	251·2	149·95	100·5 mm.
Final press. . . .	685·35	458·35	248·7	148·90	97·7 mm.
Ammonia	1·55	1·08	1·0	0·7	2·35 vol.

G. Falckenberg studied the formation and decomposition of ammonia in the silent electrical discharge.

W. R. Grove found that ammonia is decomposed by an electrically heated wire, and J. Plücker showed that the effect is merely thermal, not electrical. E. Warburg and E. Regener studied the effect of rays of short wave-length; and H. Coehn and G. Pringent, H. S. Taylor, and D. Berthelot and H. Gaudechon, the effect of ultra-violet light. In neither case does the effect appear to favour the synthesis of ammonia from its elements—*vide infra*. C. Montemartini observed the formation of ammonia from its elements in the corona discharge. H. S. Hirst detected traces of ammonia and hydrazine in the products of the reaction between nitrogen and hydrogen when exposed in silica tubes to ultra-violet light. A. C. G. Mitchell and R. G. Dickinson found that the decomposition of ammonia was effected by light of wave-length 2537A, and is sensitized by the presence of mercury vapour. For the synthesis of ammonia by the action of atomic hydrogen on nitrogen, *vide supra*, nitrogen.

F. Kuhlmann observed no sign of the formation of ammonia when a mixture of one vol. of nitrogen with 3 vols. of hydrogen is passed through a red-hot tube, even in the presence of spongy platinum. G. S. Johnson's observation to the contrary was shown by L. T. Wright, and H. B. Baker to be mal-inference due to the use of an unsuspected impurity in the nitrogen employed—namely, nitric oxide. M. Berthelot heated the 1 : 3 mixture, under diminished press., in a quartz tube at 1300°, for an hour, but observed no sign of the formation of ammonia, even when the tube was rapidly cooled. E. B. Maxted, and H. Tominaga observed the formation of ammonia and nitric oxide when a mixture of hydrogen and nitrogen is heated under 30 atm. press. by the oxyhydrogen flame. The water produced is probably dissociated, forming nitric oxide which is reduced by hydrogen to ammonia—*vide* the oxidation of nitrogen. M. Guichard, A. T. Larson and co-workers, R. S. Tour, and W. W. Scott studied the suitability of various catalysts. M. Guichard found that the addition of magnesia or nickel, tungsten, and molybdenum, and a combination of two of these metals, ensures greater catalytic efficiency. Iron-molybdenum was proved to be the most resistant and to give the highest ammonia concentration—more than 4 per cent. Iron alone gave less than 1 per cent., molybdenum less than 1·5 per cent., nickel 3 per cent., and cobalt 3 per cent. The best method of preparation is by precipitation of ferric nitrate with ammonium molybdate, followed by ignition, and subsequent reduction. With perfectly dry gases, uranium is a suitable catalyst, but its combinations with cobalt or molybdenum are of inferior value as catalysts. Uranium-nickel gives poor results, and uranium-tungsten is practically inert. R. N. Pease and H. S. Taylor found that a mixture of iron and molybdenum is a better catalyst for the ammonia reaction than is the case with either alone. H. Harter and J. M. Meyer used platinized pumice soaked in ammonium tungstate as catalyst. The Nitrogen Corporation obtained a catalyst by soaking pumice-stone in barium and calcium ferrocyanides and subsequently drying and igniting the mass ; L. Duparc and C. Urfer used the mixture obtained by heating aluminium or magnesium with an oxide of lithium, calcium, barium, strontium, beryllium, titanium, vanadium, molybdenum, or uranium. According to S. L. Tingley, ammonia is produced by passing nitrogen and hydrogen under press. through a liquid composition of mercury and osmium at a temp. below the b.p. of mercury, the press. being less than 200 atm. R. W. G. Wyckoff and E. D. Crittenden studied the X-radiograms of some ammonia catalysts. E. Baur did not induce hydrogen and nitrogen to form any ammonia by passing the mixed gases over platinum-black at 100°, or over chromium or molybdenum nitrides, or by leaving the two gases over platinized-platinum foil in the presence of hydrochloric acid. F. de la Roche, and J. B. Biot confined a mixture of hydrogen and nitrogen by mercury, having a stratum of dil. nitric acid on its surface, and sunk the vessel 540 metres in the sea. This would be eq. to a press. of about 50 atm., but no ammonia was formed. F. Varrentrapp and H. Will stated that ammonia is formed when the mixed gases are passed through a tube containing soda-lime, and if lampblack, or a mixture of carbonized potassium tartrate and lime be used, the synthesis occurs at a low temp. H. Fleck said that when a mixture of nitrogen, steam, and carbon monoxide is passed over calcium hydroxide at a dull red-heat, 5 mgrms. of ammonia are produced per 500 litres of air. R. Weinmann denied this. O. Loew, and F. Wöhler found that ammonia (and a trace of nitrate or nitrite) is formed when a mixture of nitrogen and hydrogen is passed over platinum-black moistened with a little potash-lye ; and O. Loew and K. Aso found that if the platinum-black is moistened with water, ammonia is slowly formed. L. Brunel and P. Woog did not synthesize ammonia by passing the constituent gases over a mixture of thorium and cerium oxides, palladinized-pumice, quicklime, soda-lime, calcium chloride, calcium molybdate, barium or strontium oxide, manganese dioxide, aluminium phosphate, or magnesium phosphate at 15°–350°. There is a trace of ammonia formed with nickel sesquioxide as catalyst at 180°–200° ; and with air and hydrogen, over nickel sesquioxide at 200°–240°, small quantities of ammonia are continuously formed. P. Neogi and B. B. Adhicary observed no ammonia is produced when a mixture of hydrogen and nitrogen is passed over reduced iron at a temp. varying from dull to bright redness. A negative result was also obtained with iron or nickel wire, electrolytic nickel, reduced nickel, or ferric oxide. W. A. Noyes, and H. C. Woltereck obtained ammonia by passing the mixed gases over thin layers of iron spread on asbestos at 550°; iron oxide gave a better result, and similar results were obtained with the oxides of nickel, cobalt, copper, cadmium, silver, lead, bismuth, and chromium. The reaction is continuous if air be used in place of nitrogen. 300°–350° is the most favourable temp. with iron oxide. The reaction also takes place with charcoal, coke, or peat as catalytic agent.

E. Royer and E. Jacquémin made ammonia by passing a mixture of steam and hydrogen over white-hot carbon; S. L. Tingley passed steam and nitrogen over heated calcium carbide; and L. I. de Nagy Ilosva, and M. Berthelot obtained ammonium nitrite and nitrate during the combustion of a mixture of nitrogen, oxygen, and hydrogen in excess; and also during the combustion of organic substances in air. H. W. Blackburn and W. Thomas passed nitrogen and steam, at about 2 atm. press., over a heated catalyst—*e.g.* iron at 500°: iron and nickel at 1000°; nickel oxide at 400°; ferrous oxide at 400°; or charcoal at about 800°. P. R. de Lambilly found that if a mixture of nitrogen, hydrogen, steam, and carbon monoxide is passed over pumice-stone, bone-black, or spongy platinum, ammonium formate is produced: $N_2+3H_2+2CO+2H_2O=2H.COONH_4$; while if carbon dioxide be employed, ammonium hydrocarbonate results: $N_2+3H_2+2CO_2+2H_2O=2NH_4HCO_3$. In applying these reactions on a large scale, the gases can be obtained by the alternate action of air and steam on white-hot coke, and, according to the product desired, carbon monoxide or dioxide is removed from the gas mixture to be treated. Spongy platinum was found to be the best catalyst, and a temp. of 80°–130° most suitable for the formate, and 40°–60° for the hydrocarbonate. J. Schlutius exposed a mixture of steam and producer gas (14 per cent. H_2; 43, N_2; 39, CO; and 4, CO_2) to the action of a silent discharge in the presence of platinum, and obtained ammonium formate above 80°; and ammonia, below that temp.

J. Priestley found that ammonia is decomposed into its elements when passed through a red-hot glass tube; A. B. Berthollet obtained a similar result using a porcelain tube; and H. St. C. Deville and L. Troost obtained a 75·8 per cent. decomposition at 1100°. J. M. Crafts obtained a 30 per cent. decomposition after 7–8 minutes' heating. J. Bouis, and L. J. Thénard found the decomposition is more marked if the tube be packed with fragments of porcelain or pumice-stone. A. H. White and W. Melville say that the decomposition begins at about 450°. H. C. Woltereck said that the first signs of dissociation with dry ammonia occur at 620°, and that if traces of moisture or organic matter be present, dissociation occurs at a lower temp.; in the presence of heated iron gauze, decomposition commenced at 320°; and with ferric oxide, no decomposition occurred below 420°. M. Berthelot found that the decomposition is slow at 600°, and faster at 800°. The decomposition is complete at 1300°. W. Ramsay and S. Young said that the reaction begins at 500°, and is almost complete at 780°; and the degree of decomposition attained is determined by the velocity at which the gas is passed through the hot tube. According to A. T. Larson and co-workers, when ammonia gas is decomposed into its elements by passing it over hot steel wool, at first the decomposition is slow, but later as the steel wool becomes sufficiently activated the greater portion of the gas is decomposed on its surface, and the free ammonia in the exit gases falls to about 0·01 per cent. M. Bonet y Bonfill believed that the presence of lime favours the decomposition, but J. Bouis could not confirm this. K. von Than showed that indifferent gases hinder the decomposition so much that with ammonia alone at a bright red-heat, 14·08 per cent. was decomposed, whereas in the presence of steam, 0·35 per cent. was decomposed, and in the presence of mercury vapour, 0·68 per cent. A. H. White and W. Melville observed that the rate of decomposition is increased a little in the presence of carbon monoxide or water-vapour ; and that a little cyanogen is formed in the case of carbon monoxide—more with dry than with moist gases. L. J. Thénard, and A. B. Berthollet found that the decomposition occurs more readily in the presence of platinum, gold, silver, copper, or iron. K. von Than observed no reaction in the presence of mercury at 350°. E. P. Perman and co-workers stated that ammonia can be synthesized by heating the mixed elemental gases in the presence of metals—*e.g.* iron, copper, nickel, zinc, cobalt, palladium, aluminium, and magnesium—but metals which readily form nitrides—*e.g.* magnesium—are not more active than other metals, and hence nitrides are not an intermediate stage in the formation of ammonia. The action of various metals was studied by E. P. Perman and C. A. S. Atkinson, M. Berthelot, F. Haber and co-workers, etc. As L. J. Thénard has shown, the metals undergo no noticeable change in weight, but copper and iron become brittle while gold and platinum remain unchanged. The decomposition of ammonia in the presence of platinum was studied by F. H. Constable. E. C. C. Baly and H. M. Duncan observed what they considered to be two different mol. phases of ammonia exist possessing different energy contents and reactivities, that of lower energy content being identical with completely dry ammonia. They found that the decomposition of ammonia by means of a heated, activated platinum wire gives constant values for the same amount of energy with an *active* form of the gas derived either by slow evaporation from a cylinder of compressed gas, or by gently heating the concentrated aq. soln., the gas being dried by quicklime, or by evaporating isothermally at the b.p. the gas obtained by either of these methods. A second *inactive* type, obtained by rapid evaporation of the liquefied gas, gives much smaller decomposition values under the same conditions. On standing in contact with the liquefied gas, or by heating to 200° with a platinum wire, this type slowly becomes active. The ratio of the decomposition values obtained by a first and second exposure of the gas to the heated wire differs markedly in the two forms. The addition of water vapour increases the reactivity of ammonia proportionally to the amount of water present, an increase which is lost on drying with quicklime. According to E. P. Perman, ammonia is formed by exploding the constituent elements with oxygen. The gas cannot be decomposed by heat, and therefore the reaction is not reversible ; on the contrary, M. Berthelot, and many others, have studied the reversibility of the reaction.

The equilibrium conditions of the reversible reaction: $N_2+3H_2 \rightleftharpoons 2NH_3$, or $\frac{1}{2}N_2+1\frac{1}{2}H_2 \rightleftharpoons NH_3$, were established by F. Haber and G. van Oordt. If the bracketed symbols denote the partial press. of the respective gases, $[NH_3]^2=K_p[N_2][H_2]^3$, where K_p denotes the equilibrium constant at constant press., the conc. of the amount present depends on the press. and on the temp. In studying the reaction, the equilibrium is only slowly attained at low temp., consequently F. Haber and G. van Oordt employed iron and nickel as catalytic agents ; and F. Haber and R. le Rossignol, iron, manganese, nickel, and chromium. The results showed that with 1 : 3, gas mixture, at atm. press., for equilibrium :

K_p	700°	750°	800°	850°	930°	1000°
	c. 0·00068	0·000468	0·000334	0·000279	0·000200	0·000148
NH_3	c. 0·0221	0·0152	0·0109	0·0091	0·0065	0·0048 per cent. vol.

It follows from the equilibrium equation that *the maximum conc. of ammonia at equilibrium is obtained when the hydrogen and nitrogen are present in the proportions three to one by volume.* The reaction is exothermal at ordinary temp.—being 11·89 Cals. per mol ammonia—so that the effect of raising the *temperature* will be to decrease the conc. of the ammonia. To keep the conc. of the ammonia high, the temp. of the reaction should be low ; but the reaction is then too slow for industrial work unless a suitable catalytic agent can be found. W. Nernst, and F. Jost obtained rather lower results, due, according to F. Haber and R. le Rossignol, to the mixtures referred to by W. Nernst, and F. Jost not being in equilibrium. E. B. Maxted found that mixtures of hydrogen and nitrogen furnished 0 and

3 per cent. of ammonia, when the gases are in contact with an arc at 3000°, Fig. 21. E. Briner and co-workers, E. Maurer, S. Dushman, and R. O. E. Davis and L. B. Olmstead have studied this subject. The equation for the influence of temp. on the equilibrium conc. of ammonia, deduced from these observations, is $\log_{10} K_p = 2098T^{-1} - 2\cdot5088 \log_{10} T + 0\cdot0001006T + 0\cdot0_6186T^2 + 2\cdot1$; or, approximately, $\log_{10} K_p = 2888T - 6\cdot134$. R. S. Tour has made a study of the graphs of this equation.

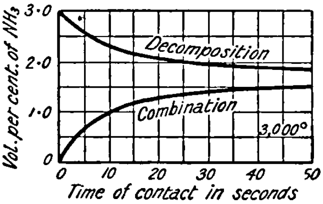

FIG. 21.—The Effect of Time on the Reaction at 3000°.

G. E. Foxwell studied the thermal decomposition of ammonia diluted with coal-gas in silica tubes packed with porous materials like coke or firebrick, and at temp. between 520° and 850°. When an excess of solid surface is present the decomposition is bimolecular. The velocity of decomposition, when the tube is filled with coke, increases slowly with increasing temp., the temp. coeff. being 1·136. The value of the velocity constant, k, may be expressed by the formula $k_2 = k_1 eA(1/T_1 - 1/T_2)$, where A is 13,300. For tubes with a radius less than 0·5 cm., k varies inversely as the square of the radius, but it is probable that for wider tubes k varies inversely as the radius. When gases containing ammonia are passed through porous material, the amount of decomposition in unit time varies directly as the square of the radius of the pores; hence it is the size of the pores rather than the total porosity that is of importance. Silica bricks have considerably less decomposing effect than siliceous (80 per cent. SiO_2) bricks, whilst the presence of iron is very deleterious. The composition of the ash of the coke affects the rate of decomposition. Rutile and orthoclase have very little, if any, action; iron pyrites is converted into ferrous sulphide during carbonization, and this increases the velocity of decomposition to some extent. Iron oxide, which is converted into metallic iron, enormously increases the rate of decomposition, and the same is true, although to a less extent, of lime. The value of k for coke is found to be 0·00200 at 755°. G. F. Uhde obtained a catalyst by heating a mixture of aluminium chloride and potassium ferrocyanide.

The above equation shows that at a constant pressure the concentration of the ammonia decreases with a rise of temperature, which allows for the variation of the thermal value of the reaction with temp. At 27°, the conc. of the ammonia at equilibrium will approach 96·32 per cent., so that a good yield of ammonia could be obtained, by direct synthesis from its elements, if a suitable stimulant could be found. For J. Lipsky's observations on the catalytic effects of cerium hydride and nitride, *vide supra,* cerium nitride. Even with the best catalyst known it is difficult to obtain satisfactory results below 500°, and it is not necessary to work over 700° since equilibrium is attained quickly enough just below this temp. E. B. Maxted has said: "It must be borne in mind that, as the synthesis of ammonia is usually carried out, the percentage of ammonia formed during the passage of the gas through the catalyst never approaches the equilibrium value for the temp. and press. used, and thus, within limits, of course, reaction velocity plays an even more important *rôle* in the determination of the amount of ammonia formed during the time of contact than the absolute value of the equilibrium ammonia percentage. If, on the other hand, the temp. employed be so high that the desired percentage of ammonia unduly approaches the equilibrium percentage, the increase in the reaction velocity due to increased temp. will no longer compensate for the decreased equilibrium ammonia content." The proportion of ammonia in the mixture of gases in equilibrium at different temp., computed by E. B. Maxted, is plotted in Fig. 22. An

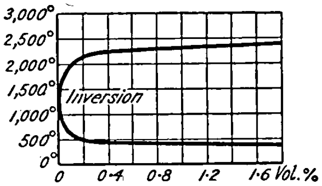

FIG. 22.—Effect of Temperature on the Equilibrium Concentration of Ammonia.

inversion occurs at about 1200°, so that above this temp., the yield of ammonia should increase with rise of temp. This was confirmed experimentally by E. B. Maxted; and A. Fowler and C. C. L. Gregory's observations of ammonia in the solar spectrum lends support to these results. E. Briner pointed out that when working at very high temp., the equilibrium formula applicable at lower temp. may have to be modified because of the dissociation of, say, hydrogen and nitrogen into atoms, and the extra production of, say, ammonia, may be due to the greater kinetic energy of the free atoms of hydrogen and nitrogen. To find the effect of *pressure*, let p denote the total press. of the gas, and C the fraction of the total vol. which each gas forms at equilibrium, it follows that $[NH_3]=pC_{NH_3}$; $[N_2]=pC_{N_2}$; and $[H_2]=pC_{H_2}$, substituting these values in the equilibrium equation, $C_{NH_3}/C^{\frac{1}{2}}{}_{N_2}C^{\frac{3}{2}}{}_{H_2}=pK_p$. When the conc. of the ammonia is small, the product $C^{\frac{1}{2}}{}_{N_2}C^{\frac{3}{2}}{}_{H_2}$ will be almost constant. Hence, the conc. of the ammonia at equilibrium will be nearly proportional to the total press. Hence, raising the press. 30 atm. should increase the conc. of the ammonia 30-fold. With the 3 : 1 gas mixture, *the concentration of the ammonia at a given temperature increases with rise of pressure.* The effect of pressure is indicated in Table XII, by F. Haber and R. le Rossignol.

TABLE XII.—EFFECT OF PRESSURE AND TEMPERATURE ON THE EQUILIBRIUM CONCENTRATION OF AMMONIA.

Temp.	Pressures.				
	1 atm.	30 atm.	100 atm.	200 atm.	1000 atm.
200°	15·30	67·6	80·6	85·8	—
300°	2·18	31·8	52·1	62·8	—
400°	0·48	10·7	25·10	36·3	—
500°	0·129	3·62	10·40	17·6	—
550°	—	—	7·00	12·2	40 (536°)
600°	0·049	1·43	4·47	8·25	30 (607°)
650°	—	—	3·00	5·8	20 (672°)
700°	0·0223	0·66	2·14	4·11	—
750°	0·0159	—	1·54	2·99	14 (740°)
800°	0·0117	0·35	1·15	2·24	—
850°	0·0089	—	0·874	1·68	—
900°	0·0069	0·21	0·68	1·34	—
950°	0·0055	—	0·542	1·07	—
1000°	0·0044	0·13	0·44	0·87	—

The last column is due to G. Claude. Some results at other press. were obtained by E. Briner and co-workers, and M. Guichard. W. Moldenhauer found the yields with increased press. agree well with the calculated values at 740° and 1000 atm. press. At lower temp., the discrepancies increase as the temp. falls and the press. rises. They are attributed to differences in the compressibilities of the different gases. G. Claude's process was described by J. H. West, and H. V. Tartar and M. F. Perkins; and R. Schönfelder concluded from an examination of the different industrial processes that G. Claude's process is the most efficient. M. Lheure, and F. Meyer described this process. S. W. Saunders obtained not so good results with $\log K_p=4790T^{-1}-5{\cdot}38\log T+0{\cdot}0001225T+0{\cdot}0_61569T^2-0{\cdot}8$, where $K_p=p^2{}_{NH_3}/p^3{}_{H_2}p_{N_2}$, as with $\log K_p=4686T^{-1}-3{\cdot}5\log T+0{\cdot}0001225T+0{\cdot}0_61569T^2-0{\cdot}8$. A. T. Larson and co-workers found that percentages of ammonia in the equilibrium conditions of $\frac{1}{2}N_2+1\frac{1}{2}H_2 \rightleftharpoons NH_3$—pressures in atm.—are:

Press.	10	30	50	100	300	600	1000
200° .	50·66	67·56	74·38	81·54	89·94	95·37	98·29
300° .	14·73	30·25	39·41	52·04	70·96	84·21	92·55
400° .	3·85	10·15	15·27	25·12	47·00	65·20	79·82
500° .	1·21	3·49	5·56	10·61	26·44	42·15	57·47
600° .	0·49	1·89	2·25	4·52	13·77	23·10	31·43
700° .	0·23	0·68	1·05	2·18	7·28	12·60	12·87

The values of the equilibrium constant are represented by $\log K_p=aT^{-1}+b\log T+cT+dT^2+I$, where $p_{\mathrm{NH}_3}=K_pP_{\mathrm{N}_2}\tfrac{1}{2}p_{\mathrm{H}_2}$, and

Atm. press.	*a*	*b*	*c*	*d*	*I*
10	2074·8	−2·4943	0	$1{\cdot}856\times10^{-7}$	1·993
30	2074·8	−2·4943	$-3{\cdot}4\times10^{-5}$	$1{\cdot}856\times10^{\ 7}$	2·021
50	2074·8	−2·4943	$-1{\cdot}256\times10^{-4}$	$1{\cdot}856\times10^{-7}$	2·090
100	2074·8	−2·4943	$-1{\cdot}256\times10^{-4}$	$1{\cdot}856\times10^{-7}$	2·113
300	2074·8	−2·4943	$-1{\cdot}256\times10^{-4}$	$1{\cdot}856\times10^{-7}$	2·206
600	2074·8	−2·4943	$-1{\cdot}0856\times10^{-3}$	$1{\cdot}856\times10^{-7}$	3·059
1000	2074·8	−2·4943	$-2{\cdot}6833\times10^{\ 3}$	$1{\cdot}856\times10^{-7}$	4·473

L. S. Gillespie represented the equilibrium constant, K_p, for temp. between 325° and 500°, and from 100 atm. to the lowest press., by $\log K_p=(2679{\cdot}35+1{\cdot}1184_p)T^{-1}-(5{\cdot}8833+0{\cdot}001232p)$; and for higher press. by $\log K_p=(2172{\cdot}26+1{\cdot}99082p)T^{-1}$. W. G. Shilling gave $\log K_p=-2068T^{-1}-2{\cdot}9278\log T+0{\cdot}0_32756T+0{\cdot}0_7513T^2+3{\cdot}1490$. This subject was studied by F. G. Keyes; and A. F. Benton investigated the kinetics of reactions in flow systems. R. E. Burk measured the rate of decomposition of ammonia by a heated molybdenum wire.

M. Bodenstein and F. Kranendieck showed that the decomposition of ammonia in quartz vessels is a surface reaction. It is inferred that the decomposition of the ammonia takes place in the pores of the quartz glass, and that the velocity of the change is determined by the rate at which the ammonia diffuses into the pores. The actual decomposition probably occurs very rapidly, but the speed of the chemical reaction is determined to some extent by the velocity with which the products of decomposition escape from the pores in the quartz into the space occupied by the gas. C. N. Hinshelwood and R. E. Burk found that the thermal decomposition of ammonia in quartz vessels, and on the surfaces of heated platinum and tungsten wires, is in equilibrium with almost complete decomposition. The reaction on the silica surface is of the first order with respect to ammonia, and it is strongly retarded by hydrogen. They found that the nature of the silica surface has a marked effect on the temp. of the reaction. They observed that in suitable silica vessels (1) the added hydrogen may have just as large a retarding effect as hydrogen formed *in situ* by the reaction, (2) the temp. coefficient may be very high, and (3) the retarding influence of the products may be constant over a range of 200°. The reaction on a heated platinum wire is of the first order as regards ammonia, and is retarded by hydrogen, but differently from the retardation in the case of silica, the equation being $d[\mathrm{NH}_3]dt=k[\mathrm{NH}_3]^n/[\mathrm{H}_2]$, where n is approximately equal to 1. Nitrogen has practically no effect on this reaction, which corresponds with a heat of activation of 140,000 cals. The reaction on a heated tungsten wire is of zero order with respect to ammonia, and is uninfluenced by the products of reaction It is much more rapid than with platinum, but the temp. coeff. is smaller and corresponds with a heat of activation of 38,700 cals.

In 1901, H. le Chatelier, reasoning from the law of mass action, showed that ammonia could be synthesized by heating above dull redness a mixture of hydrogen and nitrogen under press. in the presence or absence of spongy platinum, or finely divided iron. The industrial applications of the facts were covered by a patent which was allowed to lapse. G. Claude has devised a plant for increasing the yield of ammonia by working at a very high press., say 900–1000 atm. While the gas passing from the catalyst has ammonia corresponding, at 200 atm. press., with a 13 per cent. yield, at 1000 atm., there is a 40 per cent. yield. F. W. de Jahn claimed to have improved F. Haber's process by working at 520°–540° under a press. of 80–90 atm. over a catalyst formed by igniting a salt of cobalt, nickel, manganese, titanium, cerium, boron, uranium, or silicon upon a carrier of pumice-stone, and, after reduction in hydrogen, heating the product in contact with metallic sodium and anhydrous ammonia at 300°. With the catalyst prepared from a nickel salt, 4·5 per cent. by vol. of ammonia was obtained.

Although many important details are judiciously reserved as trade secrets, the general features of **F. Haber's ammonia process** appear to involve the preparation of nitrogen of a high degree of purity from liquid air. The reaction chamber, illustrated diagrammatically in Fig. 23, consists of a thin steel or wrought-iron tube, *A*, inside of which is a glass or fused quartz tube, *B*, narrowed towards the lower end so as to retain the catalyst, *C*, between asbestos plugs. The tube *A* is heated to 500°–600° by means of a coil of resistance wire *W* wound over the iron tube wrapped in a sheet of asbestos. The heating may also be done by internal combustion. The 3 : 1 gas mixture enters the reaction chamber, *viâ D*, and leaves the chamber at the bottom, *viâ E*. The reaction chamber is enclosed in a stronger steel tube, *F*, in which a high press. is maintained so as to prevent the thin steel tube *A* bursting under its internal press. over 150 atm. The mixed gases are forced through the chamber so that an ammonia conc. of about 8 per cent. is maintained. On leaving the furnace at *E*, the gases may be passed through a refrigerating system to liquefy the ammonia, or passed, while under press., through water or dil. acid to absorb the ammonia. In either case, the unconverted hydrogen and nitrogen are returned to the reaction chamber—*cf.* Fig. 24. Modifications were devised by L. Casale, G. Fauser, etc. Various plants have been described by J. R. Partington, R. S. Tour, A. Miolati, J. A. Harker, C. S. Imison and W. Russell, C. H. Jones, M. Lheure, M. Patart, A. Zambianchi, J. S. Negru and S. D. Kirkpatrick, F. A. Ernst and co-workers, and H. Schmidt.

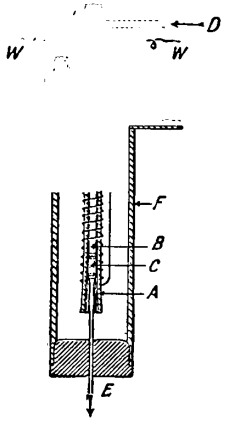

Fig. 23.—Diagrammatic Representation of the Reaction Chamber of F. Haber's Ammonia Process.

The most effective catalyst for accelerating the velocity of formation of ammonia was found to be osmium; but it is too scarce for commercial work. Next came uranium, which, in the form of carbide, crumbles to a fine powder under the conditions, and then at 500° has a high catalytic activity provided water be absent. Iron, tungsten, molybdenum, molybdic acid, ammonium molybdate, cerium, and manganese were found to be good catalysts. The catalytic activity of tungsten depends on the way it has been prepared. Platinum was found to be a poor catalyst. E. Decarrière studied palladium and platinum as catalysts; A. T. Larson and C. N. Richardson, magnetite; A. T. Otto and Sons used a metal of the iron group along with a metal oxide not easily reduced and a third substance for producing a glaze; C. Ellis, cobalt vanadate; H. Harter, a metal of the iron-group with an oxide of magnesium, titanium, thorium, vanadium, molybdenum, or tungsten; and C. H. Kunsman, a mixture of iron, aluminium, and an alkali-metal—cæsium. H. A. Bernthsen reported that certain foreign substances, *promoters*, increased the activity of the catalyst. Thus, the oxides and hydroxides of the alkalies and the alkaline earths augment the efficiency of some catalysts. A minute proportion of the promoter often suffices. A mixture of iron and potash is said to be particularly active. E. Collett used ferrites of calcium, barium, magnesium, and manganese. A comparison of uranium carbide, and the iron-potash mixture, by

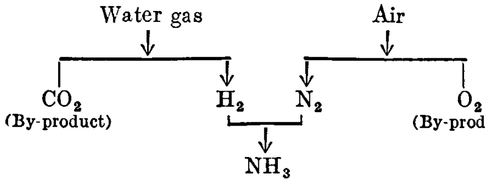

Fig. 24.—Flow Sheet of F. Haber's Ammonia Process.

F. Haber and H. C. Greenwood, and E. B. Maxted, is shown in Fig. 25. K. Inaba used iron oxide mixed with bismuth and thorium oxides as promoters; and L. H. Greathouse, a mixture of iron and manganese oxides with just enough aluminium powder to initiate the thermite reaction and fuse all the oxides. A. T. Larson used two promoters and found the joint action to be greater than either alone. Thus, an iron catalyst with alumina gave a gas with 8 per cent. of ammonia, and one with potassium oxide a gas with 5 per cent. of ammonia, whereas a mixture of the two promoters gave a gas with 14 per cent. of ammonia. A. T. Larson and A. P. Brooks found that nickel, and cobalt are inactive between 450° and 550°; molybdenum, and tungsten are most active at 550°; and iron, and a mixture of iron and molybdenum, at 450°. The action of iron is promoted by the oxides of aluminium, silicon, zirconium, thallium, cerium, and boron, but not so much so by the oxides of lanthanum, beryllium, magnesium, the alkaline earths, and alkalies. Mixtures of potassium hydroxide with alumina, silica or zirconia produced very active catalysts in conjunction with iron. J. A. Almquist and E. D. Crittenden found that the activity of iron depends on the state of oxidation of the fused oxide from which it is obtained by reduction—the magnetic oxide gave the best results. Potassium hydroxide has a marked promotor action if used in conjunction with difficultly reducible oxides like those of manganese, silicon, tungsten and aluminium, while potassium hydroxide alone lowers the activity of iron—so do the oxides of nickel and cobalt.

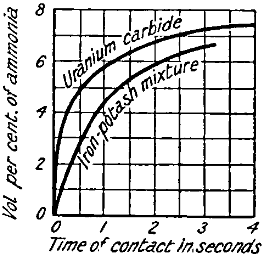

FIG. 25.—Relative Catalytic Activity of Uranium Carbide, and the Iron-potash.

A. T. Larson observed that sulphur, selenium, tellurium, phosphorus, arsenic, boron, bismuth, lead, tin, and many organic compounds act as poisons in diminishing or inhibiting the activity of the catalysts. Iron with one per cent. of sulphur is useless. One part of sulphur per million of the gas mixture is injurious. J. A. Almquist and C. A. Black found that the presence of oxygen or water-vapour reduces the activity of iron as a catalyst. E. B. Ludlam observed that the presence of hydrogen chloride slightly favours the formation of ammonia, but not so much as might be anticipated from the law of mass-action. A. Schmidt studied the action of water vapour and of hydrogen chloride. J. A. Almquist and C. A. Black found that with iron catalysts at 444° the activity is lowered by oxygen, and this the more the greater the conc. of the oxygen. Water-vapour acts similarly. E. Eloed and W. Banholzer studied the effect of varying the rate of the flow of the gas in the decomposition of ammonia by passage over a red-hot catalyst—iron, copper, or alumina. Hydrogen retards the velocity of decomposition.

C. H. Kunsman studied the thermionic properties of some catalysts; and G. B. Kistiakowsky, activation of nitrogen by catalysts by measuring its critical potentials when it is adsorbed on metal surfaces. He found two critical potentials—iron, 10·8 and 13·0 volts; nickel, 10·8 and 13·1 volts; copper, 10·8 and 13·3 volts; and platinum, 11·0 and 13·3 volts. The ionization at about 11 volts is attributed to the nitrogen atom or to a kind of excited or activated nitrogen molecule—probably the former. In agreement with the observations of L. B. Olmstead, A. W. Gauger, and J. H. Wolfenden, the ionization at 13 volts probably belongs to adsorbed hydrogen, and C. F. Fryling inferred from his observation that hydrogen on nickel is dissociated into ions. There is a critical potential at 17 volts which is attributed to molecular nitrogen, and one at 16 volts attributed to molecular hydrogen. W. A. Dew and H. S. Taylor observed a possible relation between the heat of absorption of ammonia and catalytic activity with the reaction: $2NH_3=N_2+3H_2$.

General discussions on the ammonia process for the fixation of nitrogen have been made by E. B. Maxted, *Ammonia and the Nitrides*, London, 1921; J. Knox, *The Fixation* *of Atmospheric Nitrogen*, London, 1914; H. J. M. Creighton, *How the Nitrogen Problem has been Solved*, Philadelphia, 1919; *Journ. Franklin Inst.*, 187. 377, 599, 705, 1919; F. Pope, *Refrigerating Eng.*, 12. 209, 1926; G. Fauser, *Atti Congr. Naz. Chim. Ind.*, 93, 1924; F. G. Cottrell, *Chem. Age*, 11. 282, 310, 342, 1924; F. A. Ernst, *Trans. Amer. Inst, Chem. Eng.*, , , 1926; P. Firmin, *L'Ind. Chim.*, 9. 147, 1922; J. R. Partington, in T. E. Thorpe, *Dictionary of Applied Chemistry*, London, 4. 568, 1922; P. H. S. Kempton, *Industrial Nitrogen*, London, 1922; G. Schuchardt, *Die technische Gewinnung von Stickstoff, Ammoniak und schwefelsauren Ammonium*, Stuttgart, 1919; B. Waeser, *Die Luftstickstoffindustrie*, Leipzig, 1922.

E. Baur made a gas-cell with hydrogen and nitrogen confined over a soln. of ammonia in a sat. soln. of ammonium nitrate, and obtained a current with an e.m.f. of about 0·6 volt. The hydrogen and nitrogen disappeared from the positive and negative poles in the proportion of 3 : 1 by vol. A constant e.m.f. was obtained at —10°. If a 25 per cent. soln. of ammonia in *N*-KCl was employed, no constant e.m.f. was observed. According to C. Bourdclain,[2] ammonia is formed during the rusting of iron in air; and S. Cloez observed that ammonia is formed by the slow oxidation of iron, zinc, or lead, in moist air. This observation was confirmed by W. Austin, A. Chevallier, F. Kuhlmann, and J. J. Berzelius, although M. Hall could not verify the result. A. C. Becquerel also noted that when turmeric paper is laid on plates of zinc, lead, or iron, moistened with water, the paper is reddened in places after 15 minutes' exposure; when warmed, the colour disappears. If the wetted plates are covered with white paper, and the latter after some time is introduced into a glass tube, ammonia is disengaged when heat is applied. C. P. Collard de Martigny observed that moist zinc-filings in a bottle exposed to air also produced ammonia. C. Sprengel obtained a similar result with moist smithy scales; and M. Sarzeau, with ferrous hydroxide. According to M. Faraday, large quantities of ammonia are disengaged when the hydroxide of potassium, sodium, barium, or calcium is heated with potassium, arsenic, zinc, lead, tin, or iron; smaller quantities are obtained with copper; and none at all with gold or noble metals. The ammonia is produced not only when the mixture is heated in air, but also when heated in hydrogen. G. Bischof explained the formation of ammonia in an atmosphere of hydrogen by assuming that the gas employed was not free from atm. air, and consequently of nitrogen; and J. Reiset showed that the sulphuric acid employed in the preparation of hydrogen contains nitrogen oxides. The ammonia may be formed by the action of nascent hydrogen, $Fe+3H_2O=Fe(OH)_3+3H$, either on the nitrogen of the air: $2Fe+6H_2O+N_2=2Fe(OH)_3+2NH_3$, or on the nitrates commonly present in air: $8Fe+15H_2O+3HNO_3=8Fe(OH)_3+3NH_3$—*vide infra*. The formation of ammonia in this way was doubted by H. Will. W. Thomas obtained ammonia by passing a mixture of nitrogen and steam (1 : 4) over carbon, or other catalyst, at 800°. According to E. R. Wötzcl, ammonia is formed from ionized nitrogen and nascent hydrogen obtained by passing nitrogen or flue gases through a hot bed of carbon, and then through a discharge of high-tension electricity immediately below which a jet of steam or atomized water is introduced in the same direction as the flow of the nitrogen. The gases are then cooled to condense the ammonia.

S. Peacock obtained ammonia by passing nitrogen over aluminium hydride at 400° or over. W. Austin found that a wet mixture of iron-filings and sulphur produces ammonia when exposed to air; C. F. Hollunder obtained ammonia by dropping water on a warm mixture obtained by fusing potassium polysulphide and iron-filings in air; and C. Leroy, from the liquid obtained by boiling grey antimony sulphide with a soln. of sodium carbonate in air. C. Herzog showed that ammonium sulphate is formed when water sat. with hydrogen sulphide is kept for a year in a bottle containing air. According to G. J. Mulder, ammonia is formed when a mixture of air and hydrogen sulphide is passed over pumice-stone or wood-charcoal at 30°–40°. T. Fleitmann could not verify these observations. C. Decharme said that air conducted over moist soil at 10°–52° forms ammonia, but A. Muntz and H. Condon said that the ammonia is formed in the soil by definite bacteria acting on the nitrogenous matters there present. H. Davy proved that in the electrolysis of water, with air in soln., ammonium nitrites or nitrates are formed—*vide supra;* G. Meissner obtained the same products by passing ozonized air through water; and C. F. Schönbein, by the evaporation of water in air, and the condensation of water-vapour from air. The hydrogen which escapes from some varieties of steel when fractured—*vide supra*—was supposed by M. Barré, and P. Regnard to form ammonia in contact with atm. nitrogen.

2. *The formation of ammonia by the reduction of oxygen-nitrogen compounds.*—Most gaseous nitrogen-oxygen compounds form ammonia if they are mixed with hydrogen and passed over warm platinum-sponge, platinized asbestos, or platinum-black. Thus, F. Kuhlmann[3] found that warm, not cold platinum-sponge or platinum-black converts nitrous oxide into ammonia; and M. Faraday, S. Cooke, F. Kuhlmann, P. Hare, and P. L. Dulong and L. J. Thénard found that the cold catalyst transforms nitric oxide into ammonia and water, but J. W. Döbereiner denied this. P. Sabatier and J. B. Senderens found that spongy-palladium, previously sat. with hydrogen, exerts no action on nitric oxide in the cold, but at 200°, the mass glows and ammonia and water are formed. P. Sabatier and J. B. Senderens, and P. Néogi and B. B. Adhicary studied the effect of nickel and copper in place of platinum-black. F. Kuhlmann said that when cold spongy-platinum is exposed to a mixture of hydrogen and nitric oxide or nitrogen peroxide, it becomes red hot, and frequently gives rise to a dangerous explosion; the whole of the nitrogen is converted into ammonia. Platinum-black does not act until heated to redness, and does not become incandescent. Cold spongy-platinum does not affect hydrogen saturated with the vapour of nitric acid, but when heated, it becomes red hot and converts all the nitrogen into ammonia; platinum-black does not act unless it be heated, and even then does not become incandescent in the gaseous mixture. J. Reiset said that if the mixture be passed through a red-hot tube, ammonia is obtained only when the tube contains some porous substance like pumice-stone; ferric oxide is an energetic catalyst, while the oxides of copper, zinc, and tin are less effective. He added that the catalyst is alternately reduced and oxidized. P. A. Guye and F. Schneider showed that there are probably two concurrent reactions involved in the reduction: $2NO_2+7H_2=2NH_3+4H_2O$, and $NO_2+2H_2=N+2H_2O$, and that a temp. of 250°–300° is favourable to the former when nickel is used as a catalyst. A. C. Grubb observed that when a 3 : 1-mixture of hydrogen and nitrogen is passed about an electrode at which ozonized oxygen is being rapidly evolved, ammonia is formed, due, it is assumed, to the cumulative excitation of the collisions between atoms and free electrons as indicated by O. Klein and S. Rosseland. The hydrogen appears to be excited by the ozone, and is then capable of uniting with nitrogen. R. O. Griffith and W. J. Shutt assumed that the hydrogen remains as molecular hydrogen, and reacts with ozone to form water and oxygen.

According to J. Priestley, R. Kirwan, W. Austin, and H. Davy, nitric oxide in contact with moist iron or tin-filings, or an aq. soln. of hydrogen sulphide or alkali sulphide, is reduced, forming nitrous oxide and ammonia. I. Milner found that ammonia is formed when moist nitric oxide is passed over red-hot iron-filings; and G. Ville, when a mixture of nitric oxide and hydrogen sulphide is passed over red-hot soda-lime. M. Coblens and J. E. Bernstein found that titanous chloride reduces nitric oxide, and nitrous oxide to ammonia; but not a soln. of sodium nitrite or silver hyponitrite. Ammonia is also produced when nitric acid reacts with an excess of sodium hyposulphite. According to N. A. E. Millon, and J. F. W. Johnston, some nitric or nitrous acid is reduced to ammonia when treated with hydrogen sulphide; J. Priestley found the acid to be so reduced by tin; and W. Austin, G. Fabbroni, F. Kuhlmann, and G. Bischof, by zinc, cadmium, or iron; W. Austin found that ammonia is produced by the action of zinc or iron on copper nitrate, and G. Wetzlar, by the action of iron on silver nitrate. E. Mitscherlich, and J. F. Daniell observed that a mixture of sulphuric and nitric acids can be made to dissolve zinc, iron, or tin without the evolution of gas, but ammonium sulphate is formed. F. Kuhlmann observed that ammonia is formed when a mixture of zinc and hydrochloric or sulphuric acid acts upon potassium nitrate; in the action of ferrous sulphate on nitrous acid; in the action of ferrous hydroxide, stannous hydroxide, potassium sulphide, iron sulphide, or antimony sulphide on nitrates in the presence of dil. sulphuric acid; and by the action of hydrogen sulphide on a soln. of antimony chloride and potassium nitrate. In A. Martin's process for estimating nitrates by treatment with zinc and sulphuric acid, and conversion to ammonia, there is only a partial reduction of the nitrate; A. Pavesi found that some hydroxylamine is also formed. E. Pugh found that nitrous acid is completely transformed into ammonia by the action of a soln. of stannous chloride in hydrochloric acid at 70°—*vide infra*, nitric acid. M. Görlich and M. Wichmann treated soln. of various nitrites with hydrogen sulphide, and found that the nitrogen is also quantitatively transformed into ammonia. C. Kellner reduced a soln. of sodium nitrite with sodium-amalgam and obtained ammonia. W. Müller and E. Geisenberger prepared ammonia by passing water vapour mixed with the products obtained by calcining barium or potassium nitrate, through a retort filled with carbon; and also by heating a mixture of potassium nitrate and hydroxide, and carbon. H. E. Baudoin and E. T. H. Delort found that a mixture of sodium nitrate and hydrocarbons like naphthalene or tar gives a mixture of carbon dioxide and ammonia when heated to 800°–900°.

According to R. Ihle, the formation of ammonia at the cathode in the electrolysis of nitric acid depends on the current density and the conc. of the acid. Thus, for acids of 14·67, 28·73, 43·34, and 85·37 per cent. HNO_3, current densities of 0·00159, 0·01122, and 0·0564, and 8·6 amps. per sq. cm. were respectively required before any trace of ammonia was obtained. With increased current, the quantity of ammonia formed was also increased. J. F. Daniell noted the formation of ammonia at the cathode during the electrolysis of an aq. soln. of potassium nitrate. G. E. Cassel obtained ammonia by the electrolysis of soln. of nitrates.

According to J. W. Döbereiner, if zinc together with iron be immersed in a soln. of potassium hydroxide containing a nitrate, ammonia is formed, while if the nitrate be absent, hydrogen alone is evolved. F. Schulze showed that all the nitrate- or nitrite-nitrogen is transformed into ammonia by the action of zinc, zinc and platinum, aluminium, or sodium-amalgam on alkali soln. of nitrates or nitrites. E. J. Mills and T. U. Walton found that sulphates favour the reaction; the more sulphate present the quicker the reduction. The reaction was examined by W. Wolf, A. V. Harcourt, and M. Siewert. The reaction is rather important, because upon it is based a method for determining the quantity of nitrites and nitrates in potable water.

A mixture is made of 25 grms. of sodium hydroxide in 70 c.c. of water, 20 grms. of zinc or aluminium turnings, a piece of bright sheet iron, and 5 grms. of nitric acid in a half-litre flask, ammonia gas is slowly evolved—$4Zn+7NaOH+NaNO_3=4Zn(ONa)_2+2H_2O+NH_3$, with zinc; and $8Al+5KOH+3KNO_3+2H_2O=8KAlO_2+3NH_3$, with aluminium. The reduction of the nitric acid by the hydrogen liberated by the action of zinc on the alkaline soln. is rather too slow to make this a suitable process for making ammonia for experiments with the gas. One of the methods of preparing ammonia employed by J. S. Stas, in his work on at. wts., was to allow a conc. aq. soln. of purified potassium nitrite mixed with purified potash-lye, sp. gr. 1·25, to act for 72 hrs. on an alloy of carbon-free zinc and 5 per cent. of lead and iron wire. The clear soln. was then heated until all the ammonia was expelled.

J. Reiset found that when iron-filings are heated with a conc. soln. of potassium hydroxide, at 130°, either in air or in hydrogen contaminated with nitric oxide, both nitrogen and ammonia are evolved, but if the hydrogen be thoroughly purified, no ammonia is formed. M. Faraday found no ammonia is evolved when a mixture of potassium hydroxide and nitrate is heated, but if zinc be present, ammonia is formed; J. W. Döbereiner, that a heated mixture of potassium hydroxide and nitrate and iron-filings gives off nitrogen, hydrogen, and much ammonia; and F. Kuhlmann, that sodium sulphide and potassium nitrate at 154° give off ammonia, and similar results were obtained on heating a mixture of arsenic trisulphide, potassium hydroxide and nitrate. A mixture of ethylene, alcohol vapour, or ethyl nitrate and nitric oxide furnished ammonium cyanide when passed over heated spongy-platinum. J. W. Döbereiner showed that when a soln. of platinum in aqua regia, containing some free nitric acid, is sat. with potassium hydroxide, mixed with alcohol, and exposed to sunlight, platinum-black is deposited and some ammonia is evolved. E. T. Chapman found that some ammonia is formed when nitric oxide is reduced by a conc. soln. of hydriodic acid.

The reduction of nitrates and nitrites to ammonia by the action of bacteria was observed by M. W. Beyerinck and A. van Delden,[4] E. Crespolani, M. Gerlach and I. Vogel, E. Marchal, U. Gayon and G. Dupetit, A. Müntz, and J. Stoklasa and E. Vitek—*vide supra* for the reduction to nitrogen; and for the reduction of nitrates to nitrites.

3. *The preparation of ammonia from ammoniacal compounds.*—When ammonia gas is required for the laboratory, it may be obtained from a cylinder of liquid ammonia; by boiling aqua ammonia in a flask, or by heating an intimate mixture of commercial ammonium chloride or ammonium sulphate with twice its weight of quicklime, CaO, or slaked lime, $Ca(OH)_2$. The reaction is represented: $2NH_4Cl+Ca(OH)_2=CaCl_2+2H_2O+2NH_3$. Other mixtures are recommended by C. R. Fresenius,[5] F. Mohr, and E. Harms. Ammonia combines with the ordinary drying agents—calcium chloride, sulphuric acid, phosphorus pentoxide—and accordingly these agents must not be used with the idea of drying the gas. A tower of quicklime is generally employed. R. Bunsen used fused potassium hydroxide. If a mixture of ammonium chloride and quicklime is to be heated, an iron tube, or a copper flask, without the tube-funnel, is preferable to glass, since steam is liable to condense on the walls of the flask, trickle down, and crack the hot glass. H. Hampel and H. Steinau found that ammonia is produced when iron, ammonium chloride, and nitrogen are heated together at 300° under 50 atm. press.: $3Fe+6NH_4Cl+N_2=3FeCl_2+8NH_3$. A gaseous mixture is obtained containing up to 99 per cent. of ammonia. The portion of this derived from the ammonium chloride may be allowed to react with the ferrous chloride; the ferrous hydroxide formed is reduced and the ammonium chloride recovered for further use.

J. S. Stas, in his work on at. wts., used purified ammonium chloride for the preparation of ammonia. E. Schering purified commercial aqua ammonia by distillation from an admixture with one or two per cent. of potassium permanganate, and W. N. Hartley and J. J. Dobbie removed the pyridine from ammonia by the fractional crystallization of the oxalate, and testing the product spectroscopically. C. Matignon, H. D. Gibbs, and F. G. Keyes and R. B. Brownlee, used sodium mixed with recently fused sodium chloride to purify the ammonia and distilled off the gas. L. Moser and R. Herzner said that commercial ammonium salts always contain organic matter which can be completely oxidized by nitric acid or potassium permanganate at high temp. Ammonia can be freed from pyridine and other impurities by passage over prepared wood charcoal. A. Leduc, C. Hugot, F. E. C. Scheffer, O. Brill, G. A. Burrell and I. W. Robertson obtained ammonia for their investigations by distilling aqua ammonia one or more times, and drying it with fused alkali hydroxide. The ammonia was obtained from a cylinder of the compressed gas by L. A. Elleau and W. D. Ellis, E. C. Franklin and C. A. Kraus, H. D. Gibbs, C. Dieterici and H. Drewes, P. A. Guye and A. Pintza, E. P. Perman and J. H. Davies, G. Holst, L. Moser, and E. C. McKelvy and C. S. Taylor, and fractionally distilled one or more times. A. Vogel, and T. Weyl prepared almost dry ammonia by saturating a soln. of calcium chloride with dry ammonia, and driving off the absorbed gas by heating the soln. G. Neumann obtained a steady stream of ammonia gas by the action of solid potassium hydroxide on an aq. soln. of ammonia. E. Carey and co-workers heated an intimate mixture of ammonium and sodium sulphates: $(NH_4)_2SO_4+Na_2SO_4=2NaHSO_4+2NH_3$. In his work on the liquefaction of ammonia, M. Faraday saturated silver chloride with the gas, and afterwards expelled the gas from the amminochloride (*q.v.*) by heat. J. H. Niemann used a similar process and said that a temp. of 112°–119° is necessary to drive off the ammonia. O. Knab used calcium chloride as absorbent in place of silver chloride, and H. L. F. Melsens, wood-charcoal. E. Divers and F. M. Raoult heated the liquid obtained by saturating ammonium nitrate with ammonia.

4. *The preparation of ammonia by the action of water on nitrides, etc.*—Ammonia is formed by the action of water on various nitrogen compounds (*q.v.*)—*e.g.* nitrogen phosphide, sulphide, iodide, and chloride. Its production by the action of water on various nitrides has been previously discussed. The Titan Co.[6] prepared titanium nitride by the reduction of ilmenite in an electric furnace in the presence of nitrogen, and the product treated with dil. acid to remove the iron present, was then heated with 1·3 pts. by weight of 50 per cent. sulphuric acid at 25 atm. for 3 hrs. The nitrogen present is converted into ammonium sulphate, whilst the titanium forms titanium sulphate which immediately decomposes with quantitative precipitation of titanic oxide. G. P. Guignard recommended decomposing the nitride by steam at 360°–500°. L. Mourgeon heated a metal oxide in flue gas so as to reduce the oxide, and convert the metal into nitride. The nitride was then decomposed for ammonia. The action of superheated steam on calcium cyanamide, $CaCN_2$, also furnishes ammonia: $CaCN_2+3H_2O=CaCO_3+2NH_3$. The cyanamide is made from atm. nitrogen so that this process was employed by A. Frank, and N. Caro for the fixation of nitrogen. The Stickstoffbindungs-industrie made ammonia by the action of water at 185° and 12 atm. press. on cyanides in the presence of alkali hydroxide. In the case of lithium nitride, made from atm. nitrogen: $6Li+N_2=2Li_3N$, and its subsequent treatment with water for ammonia: $Li_3N+3H_2O=3LiOH+NH_3$, the electric energy required to convert the lithium hydroxide back to lithium appears to be about half that required to oxidize the eq. quantity of nitrogen; the loss of ammonia by absorption is small. Consequently, there are many promising features in the fixation of atm. nitrogen as ammonia by the intermediate formation of nitrides of, say, lithium, barium, calcium, aluminium, etc. L. Moser and R. Herzner obtained ammonia of a high degree of purity by allowing pure magnesium or calcium nitride to fall gradually into gas-free water. Owing to the highly exothermal character of the reaction decomposition of the gas occurs if water is allowed to fall on the nitride. The only impurity is hydrogen derived from traces of metal in the nitride. B. F. Halvorsen obtained ammonia by passing a mixture of hydrogen and hydrogen cyanide along with oxygen over a heated catalyst—*e.g.* ferric or chromic oxide at about 400°. T. T. Mathieson and J. Hawliczek[7] recovered ammonia from the cyanides present in crude soda by the action of superheated steam at 300°–500°. F. Margueritte and M. de Sourvedal employed a similar process for recovering the ammonia from the cyanides produced by heating a mixture of baryta and carbon in air; and T. B. Fogarty, from the cyanide obtained by heating a mixture of powdered coke and alkali in air or in generator gas. W. A. Nelson obtained ammonia from the nitrogen of furnace gases by heating clay, or a hydrated silicate which gives off its water at a high temp. It is believed that as the water of combination is evolved, it reacts with the nitrogen or nitrogenous compounds in the furnace gases to form ammonia. This is recovered by cooling and scrubbing the furnace gases.

5. *The production of ammonia from nitrogenous organic compounds.*—The formation of ammonia from cyanides—*vide* supplementary volume. Norsk Hydro-Elektrisk Kvaelstofaktieselskab[8] obtained ammonia by the hydrolysis of hydrogen cyanide (produced in the electric arc) by means of steam; a large excess of steam is required and the process is difficult to control. If, however, the theoretical quantity of air or oxygen is added it unites with a part of the excess hydrogen present in the gas, and hydrolysis proceeds quantitatively and evenly with only a slight rise of temp., the reaction being $HCN+H_2O=NH_3+CO$. Ferric oxide or

a mixture of ferric oxide and aluminium oxide is a suitable catalyst. The surplus gases are returned to the process after enrichment and, if air has been used, its nitrogen will serve for cyanide production. As indicated in connection with the history of ammonia, *urine* and *camel's dung* are probably the oldest sources of ammonia. Putrefied urine has been used an indefinitely long time as a source of ammonia for scouring wool, etc. Normal urine has 20–25 grms. of urea or carbamide per litre, and an adult man produces 22–37 grms. of urea every 24 hrs. During the putrefaction, the urea is changed into ammonium carbonate. The above-mentioned quantity of urea (with a little uric acid) corresponds with between 9 and 17 lbs. of ammonia per man per annum. The ammonia in *sewage* is usually too dil. for it to be profitably extracted, but in a few places the ammonia is recovered from sewage and from sludge. Several patents have been taken out in this connection—*e.g.* by J. Duncan, R. Brullé and A. Leclerc, W. F. Nast, A. Mylius, K. Wedemeyer, H. W. Seiffert, F. J. Bolton and J. A. Wanklyn, J. Young, J. C. Butterfield and G. Watson, J. B. Taylor and H. V. Walker, etc. The preparation of ammoniacal liquor from leather, scraps, etc., has been discussed by T. Richters,[9] J. Young, H. Proschwitzky, L. Tralls, and L. Sternberg. Ammonia is formed when nitrogenous compounds —*leather, bones, horn, hair, skins, and other animal refuse*—are heated in closed vessels. Animal charcoal or *char* remains in the retort, while ammonia and tar rich in pyridines pass off. The tar is known as *Dippel's bone oil,* and the ammoniacal liquor which floats on the tar is then purified—*vide infra.* An old term for ammonia —*spiritus cornu cervi,* or *spirits of hartshorn*—refers to the former custom of preparing ammonia by heating the hoofs and horns of stags, etc., in closed vessels. L. N. Vauquelin [10] observed that some ammonia is formed by heating a mixture of gum and potassium nitrate; and J. S. F. Pagenstecher, a mixture of potassium nitrate and cream of tartar. F. Varrentrapp and H. Will pointed out that if potassium hydroxide or soda-lime is present, most of the nitrogen is transformed into ammonia; and E. Schulze observed that nitrogenous organic matter gives off all its nitrogen as ammonia when heated with soda-lime. This is the principle of one of the standard methods for the determination of nitrogen in organic matter. The ammonia is absorbed in sulphuric acid. The ammonia reported by J. Woodhouse, H. Davy, and C. F. Hollunder to be formed when a mixture of potassium hydroxide and charcoal is heated is probably due to the intermediate formation of cyanides from the contained nitrogen and atm. nitrogen. M. Berthelot found that many nitrogenous organic compounds furnish ammonia when heated with hydriodic acid; and J. Kjeldahl showed that the nitrogen of many nitrogenous compounds is all converted into ammonia or ammonium sulphate when heated with conc. sulphuric acid—in the case of nitro-compounds and cyanides the reaction is not always quantitative. The reaction proceeds more satisfactorily in the presence of mercury or mercuric oxide, copper, potassium hydrosulphate, sugar, phenol, benzoic acid, and analogous compounds. This reaction has been discussed by C. Arnold, A. Atterberg, C. Budde and C. V. Schon, G. Czeczetka, L. Garnier, J. W. Gunning, G. Kreusler, P. Kulisch, L. Maquenne and E. Roux, B. Proskauer and M. Zülzer, S. Schmitz, K. Ulsch, H. Vogtherr, H. Wilfarth, etc. In 1841, J. Young proposed to recover ammonia from *guano* by mixing it with lime and heating it in a closed vessel, but the process was not remunerative. G. Vibrans [11] proposed to collect the small amount of ammonia which is evolved during the evaporation of *beetroot juice* for sugar. A comparatively large proportion is present in *vinasse, i.e.* the residue left after fermenting the sugar of molasses and distilling off the alcohol. When vinasse is distilled in a closed vessel, ammonia and trimethylamine are evolved and the residue is employed as manure or worked up for potassium salts. Patents for this have been obtained by W. Bueb, Badische Gesellschaft, L. Sternberg, E. Ernst, R. Lederer and W. Gintl, E. Meyer, etc.; and the subject has been discussed by H. Ost, J. Lajbi, and C. Vincent.

Ammonia is produced as a by-product during the dry distillation of *coal* in the manufacture of *coal-gas*, and in the manufacture of *coke* in coke-ovens. Only a small percentage of the total nitrogen of the coal is recovered in the form of ammonia, the remainder is distributed in the coke, in the tar, as cyanide in the gas and ammoniacal liquor, and as free nitrogen in the gas. The percentage amounts of the total nitrogen distributed in this manner are as follow:

	Coke.	Tar.	Cyanides.	Nitrogen.	Ammonia.
Gas-works . .	58·3	3·9	1·2	19·5	17·1
Coke-ovens . .	43·31	2·98	1·43	37·12	15·6

The gas-works data are by J. McLeod;[12] and the coke-oven data, by A. Short. The maximum yield of ammonia is obtained at about 900°–950°, and the normal production is about 20–25 lbs. of ammonium sulphate per ton of coal carbonized. With low temp. carbonization, about 450°, as in the manufacture of *coalite*, a large proportion of the nitrogen remains with the coke; at higher temp., more nitrogen is given off from the coal, primarily as ammonia, yet this is subsequently decomposed by the action of the incandescent carbon. Vertical retorts working at a higher temp. may give a higher yield than horizontal retorts because in spite of the unfavourable tendency of the higher temp. to decompose the ammoniacal vapours, the volatile products escape from the hot-zone more rapidly. If the vertical retorts are steamed during carbonization, the yield may be doubled. The use of lime, recommended by W. J. Cooper, for increasing the yield of ammonia, was abandoned because of the resulting deterioration of the coke. R. A. Mott and H. J. Hodsman discussed the factors influencing the yield of ammonia in the carbonization of coal. The extraction of ammonia from coke-oven gas, etc., was discussed by M. Mayer and V. Altmayer, H. Warth, C. Winkler, L. Mond, J. Meikle, G. Claude, Z. M. Stinnes and A. Weindel, F. W. Steere, H. A. Curtis, C. H. S. Tupholme, R. R. Tatlock, W. Heinemann, G. Reiniger, T. von Bauer, etc. In the manufacture of the so-called *producer gas* from gaseous fuel, at a higher temp., much of the ammonia is dissociated in the producer, but if the temp. is kept low, by the use of steam, much of the ammonia escapes decomposition and can subsequently be recovered. This is at the expense of the calorific value of the fuel. Ammonia is present in *blast furnace gas* when coal is used. In that case, the ammonia and tar are recovered by cooling and washing the gas. Many attempts —by H. Grouven, J. Rüderer and co-workers, W. Steger, G. W. Ireland and H. S. Sugden, A. Muntz and E. Lainé, P. Kuntze, C. Pieper, L. Casale, P. Bratt, G. Claude, E. L. Pease, K. P. McElroy, and H. C. Woltereck—have been made to recover ammonia from *peat*, but with no marked success. The subject has been discussed by A. Frank and N. Caro. Ammonia is evolved in the distillation of *oil-shales*, and it can be recovered by cooling and washing. W. Young and G. T. Beilby increased the yield of ammonia by the introduction of steam during the distillation.

The ammoniacal liquor obtained by washing the gases produced by the dry distillation of nitrogenous substances is decanted from the tar. It is a pale yellow or dark brown liquid smelling strongly of ammonia, hydrogen sulphide and phenols. Its sp. gr. is 1·01–1·03. The composition of the ammoniacal liquor varies at different stages of the process—*e.g.* the hydraulic main liquor, the condenser liquor, and the scrubber and washer liquors of the gas-works—with the nature of the coal employed, the conditions of carbonization, and the nature and method of working the plant. The qualitative composition does not vary so much. The liquid contains ammonium chloride, sulphides, carbonates, cyanide, thiosulphate, thiocyanate, and ferrocyanide. Small quantities of pyridine are present, and, according to F. W. Skirrow, 0·1–0·35 grm. of phenols per 100 c.c. The percentage amounts of the above constituents present in 100 c.c. of liquid are indicated in Table XIII, by S. E. Linder. An analogous table for German coal has been made by M. Mayer and H. Hempel. There has been some discussion as to the presence

TABLE XIII.—THE COMPOSITION OF AMMONIACAL LIQUOR (Grams per 100 c.c.)

Constituent.	Gas-works.			Coke-oven.	Blast furnaces.		Shale works.	Coalite works.
	Average.	Hydraulic main.	Condenser.	Average.	Coolers.	Washers.	Average.	Average.
Volatile ammonia . . .	1·929	0·721	3·247	0·841	0·191	0·362	0·873	1·547
Fixed ammonia . . .	0·613	0·306	0·221	0·102	0·008	0·009	0·032	0·170
Total ammonia . . .	2·542	1·027	3·468	0·943	0·199	0·371	0·905	0·717
Amm. sulphide, $(NH_4)_2S$ . .	0·862	0·276	0·768	0·466	nil	—	0·098	0·230
Amm. carbonate, $(NH_4)_2CO_3$.	5·000	1·320	8·810	1·960	1·104	—	2·870	0·360
Amm. chloride, NH_4Cl . .	1·120	0·838	0·459	0·217	0·006	—	0·015	0·106
Amm. sulphate, $(NH_4)_2SO_4$.	0·202	—	—	0·032	0·009	—	0·016	0·054
Amm. thiosulphate, $(NH_4)_2S_2O_3$	0·173	—	—	0·041	0·002	—	0·090	0·407
Amm. thiocyanate, NH_4SCy .	0·528	0·047	0·070	0·043	0·003	0·003	nil	0·335
Amm. cyanide, NH_4Cy . .	0·036	0·034	0·070	0·070	nil	0·003	nil	nil
Amm. ferrocyanide, $(NH_4)_4FeCy_6$	0·038	0·089	0·030	nil	nil	nil	nil	nil

of free ammonia; in many cases, the acids produced are sufficient to combine with all the ammonia; but with hydraulic main liquor collected above 60°, free ammonia is usually present. The existence of ammonium cyanide has also been questioned.

The ammoniacal liquor was formerly neutralized with sulphuric or hydrochloric acid and the soln. evaporated for the sulphate or chloride. The products were very impure, and the escaping hydrogen sulphide, etc., created a nuisance. The ammonia is now usually recovered by distillation from an admixture of the ammoniacal liquor with lime or soda-lye. The still may be heated by external firing, by internal heating with steam-coils, or, as is the common practice, by blowing live steam through the still. The ammonia evolved may be converted into sulphate, conc. gas-liquor, aq. ammonia, or liquid ammonia. The largest proportion is converted into sulphate. Stills have been described by H. Grüneberg and E. Blum,[13] A. Feldmann, G. Wilton, P. Parrish and O. W. Wright, W. M. Scott, J. Ballantyne, W. Wyld, etc.

A. Feldmann's original process is illustrated by Fig. 26. The gas liquor passes through the rectifying column *A*, and flows into the vessel, *B*, into which milk of lime is pumped at intervals, *viâ G*. At the same time the whole is kept agitated by steam injected into the mixture. The liquor, after depositing most of the lime, flows into the second column, *C*, where the ammonia liberated by the lime is distilled off. The spent liquor runs continuously away *viâ g*, and the gases and vapours pass *viâ h* into the first column, *BA*, which serves both for retaining the water, and for driving off the volatile ammonium salts in the crude gas-liquor. The saturator, *E*, and gas-ball, *F*, require no special comment. In the more recent types, only a single column is used, and modifications have been made in the method of introducing the milk of lime.

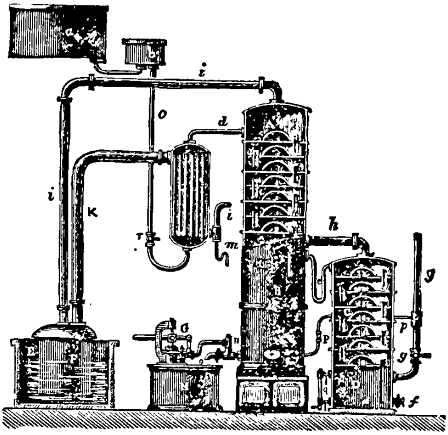

FIG. 26.—A. Feldmann's Ammonia Still.

Ammonia was formerly obtained by distilling a mixture of ammonium sulphate and lime; but it is now usually made by direct distillation of the gas-liquor so as to produce either the so-called *concentrated gas-liquor*, or the so-called *caustic ammonia*. The former has 16–26 per cent. of ammonia in the cruder product containing the sulphide, and sometimes the carbonate. It is used for the preparation of ammonium salts, and in the ammonio-soda process. To prepare caustic ammonia, a large excess of lime must be added to the gas-liquor to hold back the acid constituents including carbon dioxide and hydrogen sulphide; or, as is more usual, the vapours are passed through a set of two or three washers containing milk of lime. The last lime-washer may contain a little ferrous sulphate in soln. to remove the last traces of sulphur, or else, as recommended by O. Pfeiffer, a small extra washer containing soda-lye is added. Different types of washers have been recommended. The gases then pass through a series of scrubbers charged with wood-charcoal to remove the strong-smelling, empyreumatical matter derived from the tar—in some cases the gases are finally passed through a fatty or high boiling mineral oil to remove these empyreumatical matters. The sat. charcoal is revivified for use by heating in closed retorts. The purified gas is finally passed into distilled water to form aqua ammonia of any conc. up to 36 per cent. NH_3.

The subject has been discussed in the following works: G. T. Calvert, *The Manufacture of Sulphate of Ammonia*, London, 1911; J. Grossmann, *Das Ammoniak und seine Verbindungen*, Halle a. S., 1908; F. Muhlert, *Die Industrie der Ammoniak und Cyanverbindungen*, Leipzig, 1915; R. Arnold, *Ammonia and Ammonium Compounds*, London, 1890; V. Urbain, *Ammoniaque*, Paris, 1884; C. A. T. Villiers, *Ammonium et les sels ammoniacaux*, Paris, 1884; P. Truchot, *L'ammoniaque, ses nouveaux procédés de fabrication*, Paris, 1897; G. Schuchardt, *Die technische Gewinnung von Stickstoff, Ammoniak, und schwefelsäurem Ammonium*, Stuttgart, 1919.

In addition to the aqua ammonia of commerce, the gas is liquefied and stored in steel cylinders. Liquid ammonia is used for refrigeration. Instead of passing the gas into water, it is well dried, and liquefied by compression pumps. H. W. Foote and S. R. Brinkley[14] recommended the following method of storing and delivering dry ammonia:

The apparatus consists of a 500 c.c. wide-necked bottle fitted with a stopper carrying two tubes with taps, one for delivery and the other for charging. The bottle is nearly filled with dry ammonium thiocyanate, which acts as adsorbent. The bottle is surrounded by ice and the charging tube connected to an ammonia generator, the ammonia as it enters the bottle is absorbed about as rapidly as by water, and when the ammonium thiocyanate is sat., it contains about 45 per cent. of its wt. of ammonia. The ammonia can be drawn off by slightly raising the temp., room temp. is generally sufficiently high. This method has the advantages that the rate of evolution of the gas can be readily controlled by slight changes of temp., and also the gas evolved is dry.

According to E. Schering, some commercial samples of aqua ammonia contain ammonium carbonate, chloride, and thiocyanate, as well as pyridine, pyrrol, etc. Hence, with acetic acid, it may acquire a yellow colour, and with hydrochloric acid a red colour. H. von Strombeck reported the residue left on evaporating some samples of liquid ammonia contained water; methyl, ethyl, and isopropyl alcohols; acetone; and ammonium carbonate. In addition, mineral oil, sand, and iron oxide and sulphide were found, being accidental impurities introduced during liquefaction or from the iron containers. A. Lange and J. Hertz reported water, pyridine and some of its homologues, nicotine, ethyl alcohol, acetonitrile, ammonium carbonate, and mineral oil—and occasionally benzene and naphthalene—but they never found acetone or any alcohols other than ethyl alcohol. K. Urban reported pyrrol. J. Bougault and B. Gros found acetone. The non-condensing gases in the container were found by W. D. Richardson, and F. W. Frerichs to be mainly oxygen and nitrogen nearly in the proportions required for air; and, in some cases, hydrogen was present. A. Lange, E. C. McKelvy and C. S. Taylor, C. Ludeking and J. E. Starr, H. Bunte and P. Eitner, and R. Lucion and D. de Paepe have made observations on this subject. For the purification of ammonia from the cylinders, *vide supra.*

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§ 16. The Physical Properties of Ammonia

Ammonia is a colourless gas with a pungent odour, and an alkaline taste. If inhaled suddenly, it will bring tears to the eyes; if large quantities be inhaled, suffocation may ensue. Ammonia can be condensed to a colourless, mobile liquid, and frozen to a white solid. H. E. Behnken [1] found that the **crystals** belong to the cubic system. H. Mark and E. Pohland said that the **X-radiogram** of ammonia between —77° and —160°, shows that the unit cube has 4 molecules of ammonia, and that the edge of the cube is 5·19 A. in length. J. de Smedt obtained 5·12 A. for the edge of unit cube. R. Brill said that the lattice resembles that of lithium nitride, Li_3N. As a gas, it is a little more than half as heavy as air, and consequently, the gas is collected, like hydrogen, by the downward displacement of air; the suggestion has been made to use ammonia instead of hydrogen for inflating airships. The lifting power of hydrogen is 2·3 times as great as that of ammonia, and it is but $\frac{1}{10}$th the cost; ammonia has a greater corroding action on the balloon envelope. Against these very serious disadvantages, ammonia is less inflammable, and, as liquid ammonia, it is more portable. H. Davy gave 0·5901 for the **vapour density** of ammonia—air unity; T. Thomson, 0·5931; J. B. Biot and F. J. Arago, 0·5967; and A. Leduc, 0·5971 ± 0·0002. The **litre-weight** of the gas at n.p. θ, given by J. B. Biot and F. J. Arago, is 0·7752 grm.; A. Leduc, and Lord Rayleigh gave 0·7719 grm.; and P. A. Guye and A. Pintza, 0·7708 grm.—E. Moles gave 0·7715 grm. for the best representative value. E. P. Perman and J. H. Davies said that a gram of ammonia at —20° occupies 1·19575 litres; at 0°, 1·2973 litres; at 50°, 1·5473 litres; and at 100°, 1·7964 litres. They also found that at 380 mm. press., a litre of ammonia at 0° weighs 0·3832 grm. The literature was reviewed by M. S. Blanchard and S. F. Pickering. The **specific volume** and **specific gravity** of sat. ammonia vapour are indicated in Tables XIV and XV by C. S. Cragoe, E. C. McKelvy, and G. F. O'Connor.

TABLE XIV.—SPECIFIC VOLUME OF SATURATED AMMONIA VAPOUR (c.c. per gram).

θ° C.	0°	1°	2°	3°	4°	5°	6°	7°	8°	9°
—40°	1551·1	1631·0	1761·0	1806·0	1901·0	2002·0	2111·0	2226·0	2350·0	2482·0
—30°	962·5	1008·0	1056·0	1106·0	1160·0	1215·0	1274·0	1336·0	1403·0	1475·0
—20°	623·5	650·0	678·0	707·5	738·5	771·5	806·0	841·5	879·5	920·0
—10°	418·5	435·0	452·0	470·0	489·0	508·5	529·5	551·5	574·5	598·5
0°	289·7	300·1	311·0	322·5	334·4	346·9	360·0	373·6	387·9	402·8
0°	289·7	279·7	270·0	260·8	251·9	243·4	235·2	227·4	219·9	212·7
+10°	205·8	199·1	192·7	186·6	180·7	175·0	169·5	164·2	159·1	154·2
+20°	149·45	144·95	140·55	136·35	142·25	128·35	124·55	120·95	117·40	114·00
+30°	110·75	107·55	104·45	101·50	98·65	95·85	93·20	90·60	88·05	85·65
+40°	83·28	81·02	78·82	76·68	74·61	72·61	70·66	68·77	66·94	65·17

Observations were also reported by C. Ledoux, A. Berthoud, C. H. Peabody, V. Wood, G. A. Zeuner, H. Mollier, C. Dieterici, G. Wobsa, H. J. MacIntire, J. Hýbl, C. E. Lucke, G. A. Goodenough and W. E. Mosher, G. Holst, and F. G. Keyes and R. B. Brownlee. C. S. Cragoe and co-workers represented the sp. vol. of sat. ammonia vapour by $v=300(6·46344/T—0·106887+0·0356803 \log_{10}T)+0·0862366\sqrt{406·1-T}+0·002667(406·1-T)$, where v is expressed in c.c. per gram, and T in °K. The value at 60° is 48·81; at 70°, 37·78; at 80°, 29·34; at 90°, 22·75; and at 100°, 17·52. The sp. vol. of liquid ammonia was found by

TABLE XV.—DENSITY OF SATURATED AMMONIA VAPOUR (grams per litre).

θ° C.	0°	1°	2°	3°	4°	5°	6°	7°	8°	9°
—40°	0·645	0·613	0·583	0·554	0·526	0·500	0·474	0·449	0·426	0·403
—30°	1·038	0·992	0·947	0·904	0·863	0·823	0·785	0·748	0·713	0·678
—20°	1·604	1·538	1·475	1·413	1·354	1·296	1·241	1·188	1·137	1·087
—10°	2·390	2·299	2·212	2·128	2·046	1·967	1·889	1·813	1·741	1·671
0°	3·452	3·332	3·215	3·101	2·990	2·883	2·778	2·677	2·578	2·483
0°	3·452	3·575	3·702	3·834	3·970	4·109	4·252	4·398	4·548	4·702
+10°	4·860	5·023	5·189	5·359	5·534	5·714	5·900	6·090	6·285	6·485
+20°	6·690	6·900	7·115	7·335	7·560	7·791	8·028	8·270	8·518	8·771
+30°	9·030	9·295	9·570	9·850	10·140	10·435	10.735	11·040	11·355	11·680
+40°	12·010	12·345	12·690	13·040	13·400	13·770	14·150	14·540	14·940	15·345

M. Faraday to be 1·32 at 10°, and 1·368 at 15·5° ; P. Jolly, 1·604 at 0° ; G. Lunge, 1·626 at 20°; and A. Lange and J. Hertz, 1·47 at —38°. K. Urban also made a measurement. E. d'Andréeff gave 1·540 at —10° ; 1·555 at —5° ; 1·571 at 0° ; 1·588 at 5° ; 1·605 at 10° ; 1·623 at 15° ; and 1·642 at 20°. An extended series of observations were made by C. Dieterici and H. Drewes, A. Mittasch and co-workers, A. Berthoud, F. G. Keyes and R. B. Brownlee, and G. A. Goodenough and W. E. Mosher. The results of A. Berthoud are summarized in Fig. 27—*vide infra*, Fig. 29. J. H. Shaxby deduced a theoretical expression for the density and mol. diameter of liquid ammonia. The results of C. S. Cragoe and D. R. Harper are shown in Table XVI; they found that M. Avenarius' equation $v=3{\cdot}68+\log(130-\theta)$ gives

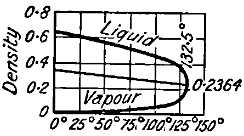

FIG. 27.—Density of Ammonia — Liquid and Vapour.

TABLE XVI.—SPECIFIC VOLUME OF LIQUID AMMONIA UNDER SATURATION PRESSURE (c.c. per gram).

θ° C.	0°	1°	2°	3°	4°	5°	6°	7°	8°	9°
—70°	1·3788	1·3766	1·3745	1·3724	1·3702	1·3681	1·3660	1·3639	1·3618	1·3597
—60°	1·4010	1·3988	1·3965	1·3942	1·3920	1·3898	1·3876	1·3854	1·3832	1·3810
—50°	1·4245	1·4221	1·4197	1·4173	1·4150	1·4126	1·4103	1·4079	1·4056	1·4033
—40°	1·4493	1·4468	1·4442	1·4417	1·4392	1·4367	1·4342	1·4318	1·4293	1·4269
—30°	1·4757	1·4730	1·4703	1·4678	1·4649	1·4623	1·4597	1·4571	1·4545	1·4519
20°	1·5037	1·5008	1·4980	1·4951	1·4923	1·4895	1·4867	1·4839	1·4811	1·4784
—10°	1·5338	1·5307	1·5276	1·5245	1·5215	1·5185	1·5155	1·5125	1·5096	1·5066
—0°	1·5660	1·5627	1·5594	1·5561	1·5528	1·5496	1·5464	1·5432	1·5400	1·5369
+0°	1·5660	1·5694	1·5727	1·5761	1·5796	1·5831	1·5866	1·5901	1·5936	1·5972
10°	1·6008	1·6045	1·6081	1·6118	1·6156	1·6193	1·6231	1·6270	1·6308	1·6347
20°	1·6386	1·6426	1·6466	1·6506	1·6547	1·6588	1·6630	1·6672	1·6714	1·6757
30°	1·6800	1·6844	1·6888	1·6932	1·6977	1·7023	1·7069	1·7115	1·7162	1·7209
40°	1·7257	1·7305	1·7354	1·7404	1·7454	1·7504	1·7555	1·7607	1·7659	1·7713
50°	1·7766	1·7820	1·7875	1·7931	1·7987	1·8044	1·8102	1·8160	1·8220	1·8280
60°	1·8341	1·8403	1·8465	1·8529	1·8593	1·8658	1·8725	1·8792	1·8860	1·8930
70°	1·9000	1·9072	1·9145	1·9219	1·9294	1·9370	1·9448	1·9528	1·9608	1·9690
80°	1·9774	1·9859	1·9946	2·0034	2·0124	2·0217	2·0311	2·0407	2·0505	2·0605
90°	2·0708	2·0813	2·0920	2·1030	2·1143	2·1258	2·1377	2·1498	2·1623	2·1752
100°	2·1885	—	—	—	—	2·261	—	—	—	—
110°	2·348	—	—	—	—	2·455	—	—	—	—
120°	2·50	—	—	—	—	2·80	—	—	—	—
130°	3·18	—	—	4·283	—	—	—	—	—	—

good results for the sp. vol. between —50° and 50°, where v denotes c.c. per gram, and θ in °C.; and they represented their results by:

$$v=\frac{4{\cdot}2830+0{\cdot}813055\sqrt{133-\theta}-0{\cdot}0082861(133-\theta)}{1+0{\cdot}424805\sqrt{133-\theta}+0{\cdot}015938(133-\theta)}$$

M. Faraday gave 0·74 at 10°, and 0·731 at 15·5° for liquid ammonia. P. Jolly gave 0·6234 at 0°/0°; and E. d'Andréeff, 0·6502 at —10·7°; 0·6362 at 0°; 0·6347 at 1·1°; 0·6288 at 5·4°; 0·6228 at 10·4°; and 0·6134 at 16·5°; J. Timmermans also measured the density of liquid ammonia; and A. Lange, the sp. gr., D, of liquid ammonia at different temp.; the change of vol., δv, per unit vol., $v=1$; and the mean coeff. of expansion; and his results are given in Table XVII. Observations by C. S. Cragoe and D. R. Harper on the density of liquid ammonia are indicated in Table XVIII. E. C. McKelvy and C. S. Taylor gave 0·817 grm. per c.c. for the density of solid ammonia at —79°; and 0·836 at —185°. C. H. Meyers and R. S. Jessup studied the sp. vol. of the sat. vapour.

TABLE XVII.—SPECIFIC GRAVITY AND THERMAL EXPANSION OF LIQUID AMMONIA.

Temp.	Sp. gr.	δv.	Coeff. exp.	Temp.	Sp. gr.	δv.	Coeff. exp.
−50°	0·6954	0·9119	—	30°	0·5918	1·0715	0·00257
−40°	0·6835	0·9277	0·00174	40°	0·5756	1·1015	0·00285
−30°	0·6715	0·9443	0·00180	50°	0·5584	1·1355	0·00313
−20°	0·6593	0·9617	0·00185	60°	0·5404	1·1735	0·00338
−10°	0·6469	0·9802	0·00194	70°	0·5213	1·2164	0·00380
0°	0·6341	1·0000	0·00204	80°	0·5004	1·2673	0·00428
10°	0·6207	1·0215	0·00217	90°	0·4774	1·3281	0·00491
20°	0·6067	1·0451	0·00234	100°	0·4522	1·4021	0·00572

TABLE XVIII.—SPECIFIC GRAVITY OF SOLUTIONS OF AMMONIA UNDER SATURATION PRESSURE (grams per c.c.).

θ° C.	0°	1°	2°	3°	4°	5°	6°	7°	8°	9°
−70°	0·7253	0·7264	0·7275	0·7287	0·7298	0·7309	0·7321	0·7332	0·7343	0·7354
−60°	0·7138	0·7149	0·7161	0·7172	0·7184	0·7195	0·7207	0·7218	0·7230	0·7241
−50°	0·7020	0·7032	0·7044	0·7056	0·7067	0·7079	0·7091	0·7103	0·7114	0·7126
−40°	0·6900	0·6912	0·6924	0·6936	0·6948	0·6960	0·6972	0·6984	0·6996	0·7008
−30°	0·6777	0·6789	0·6801	0·6814	0·6826	0·6839	0·6851	0·6863	0·6875	0·6888
−20°	0·6650	0·6663	0·6676	0·6688	0·6701	0·6714	0·6726	0·6739	0·6752	0·6764
−10°	0·6520	0·6533	0·6546	0·6559	0·6572	0·6585	0·6598	0·6611	0·6624	0·6637
− 0°	0·6386	0·6399	0·6413	0·6426	0·6440	0·6453	0·6467	0·6480	0·6493	0·6507
+ 0°	0·6386	0·6372	0·6358	0·6345	0·6331	0·6317	0·6303	0·6289	0·6275	0·6261
10°	0·6247	0·6233	0·6218	0·6204	0·6190	0·6175	0·6161	0·6146	0·6132	0·6117
20°	0·6103	0·6088	0·6073	0·6058	0·6043	0·6028	0·6013	0·5998	0·5983	0·5968
30°	0·5952	0·5037	0·5921	0·5906	0·5890	0·5875	0·5859	0·5843	0·5827	0·5811
40°	0·5795	0·5779	0·5762	0·5746	0·5729	0·5713	0·5696	0·5680	0·5663	0·5646
50°	0·5629	0·5612	0·5594	0·5577	0·5560	0·5542	0·6624	0·5507	0·5489	0·5471
60°	0·5452	0·5434	0·5416	0·5397	0·5378	0·5359	0·5341	0·5321	0·5302	0·5283
70°	0·5263	0·5243	0·5223	0·5203	0·5183	0·5163	0·5142	0·5121	0·5100	0·5079
80°	0·5057	0·5036	0·5014	0·4991	0·4696	0·4946	0·4924	0·4900	0·4877	0·4853
90°	0·4829	0·4805	0·4780	0·4755	0·4730	0·4704	0·4678	0·4652	0·4625	0·4597
100°	0·4569	0·4541	0·4512	0·4483	0·4453	0·4422	0·4391	0·4360	0·4327	0·4294
110°	0·426	—	—	—	—	0·407	—	—	—	—
120°	0·385	—	—	—	—	0·357	—	—	—	—
130°	0·315	—	—	*a*0·2335	—	—	—	—	—	—

Observations on the sp. gr. of aq. ammonia were made by J. Dalton, H. Davy, A. Ure, J. B. Richter, and J. J. Griffin, and the results for the more conc. soln. show great deviations. Tables were compiled by L. Carius, H. Hager, N. J. Price and C. S. L. Hawkins, O. Wachsmuth, H. Grüneberg, W. C. Ferguson, and J. H. Smith. G. G. and I. N. Longinescu, E. L. Nichols and A. W. Wheeler, G. T. Gerlach and H. Grüneberg, E. Baud and L. Gay, and B. S. Neuhausen and W. A. Patrick also calculated values for the sp. gr. The results of G. Lunge and J. Wiernik at 15°/4° are indicated in Table XIX. Tables for aq. soln. with 20·7, 29·9, 40·75, 42·75, 49·0, and 50·83 per cent. NH_3 at 18 temp. in the interval from 0° to 60° were calculated by A. Mitlasch and co-workers. The following is a selection from these results:

	0·3°	10·7°	20·45°	30·1°	40·0°	50·05°	60·2°
NH_3 20·7 per cent. .	0·9294	0·9249	0·9198	0·9148	0·9089	0·9026	0·8964
	0·3°	11·3°	20·5°	30·18°	39·8°	49·9°	59·9°
NH_3 29·9 per cent. .	0·9039	0·8982	0·8921	0·8860	0·8790	0·8716	0·8636
	0·50°	1·1°	11·0°	20·55°	24·3°	30·09°	39·50°
NH_3 40·75 per cent. .	0·8734	0·8730	0·8654	0·8576	0·8556	0·8499	0·8417
	0·9°	7·1°	10·630°				
NH_3 50·83 per cent. .	0·8436°	0·8380°	0·8350				

TABLE XIX.—SPECIFIC GRAVITY AND CONCENTRATION OF AQUEOUS SOLUTIONS OF AMMONIA.

Sp. gr.	NH_3		Sp. gr.	NH_3		Sp. gr.	NH_3	
	Per cent.	Grams per litre.		Per cent.	Grams per litre.		Per cent.	Grams per litre.
1·000	0·00	0·0	0·960	0·91	95·1	0·920	21·75	200·1
0·998	0·45	4·5	0·958	10·47	100·3	0·918	22·39	205·6
0·996	0·91	9·1	0·956	11·03	105·4	0·916	23·03	210·9
0·994	1·37	13·6	0·954	11·60	110·7	0·914	23·68	216·3
0·992	1·84	18·2	0·952	12·17	115·9	0·912	24·33	221·9
0·990	2·31	22·9	0·950	12·74	121·0	0·910	24·99	227·4
0·988	2·80	27·7	0·948	13·31	126·2	0·908	25·65	232·9
0·986	3·30	32·5	0·946	13·88	131·3	0·906	26·31	238·3
0·984	3·80	37·4	0·944	14·46	136·5	0·904	26·98	243·9
0·982	4·30	42·2	0·942	15·04	141·7	0·902	27·65	249·4
0·980	4·80	47·0	0·940	15·63	146·9	0·900	28·33	255·0
0·978	5·30	51·8	0·938	16·22	152·1	0·898	29·01	260·5
0·976	5·80	56·6	0·936	16·82	157·4	0·896	29·69	266·0
0·974	6·30	61·4	0·934	17·42	162·7	0·894	30·37	271·5
0·972	6·80	66·1	0·932	18·03	168·1	0·892	31·05	277·0
0·970	7·31	70·9	0·930	18·64	173·4	0·890	31·75	282·6
0·968	7·82	75·7	0·928	19·25	178·6	0·888	32·50	288·6
0·966	8·33	80·5	0·926	19·87	184·2	0·886	33·25	294·6
0·964	8·84	85·2	0·924	20·49	189·3	0·884	34·10	301·4
0·962	9·35	89·9	0·922	21·12	194·7	0·882	34·95	308·3

S. M. Delépine measured the sp. gr. of soln. of ammonia in aq. soln. of ethyl alcohol. I. Traube found the **molecular co-volume** of ammonia in aq. soln. is nearly 24·1. W. Herz, R. Lorenz and W. Herz, S. Mokruschin, E. Rabinowitsch, and E. Moles studied the mol. vol. A. O. Rankine estimated the mean **collision area** of ammonia molecules to be $0{\cdot}640\times10^{-15}$ sq. cm.; and R. S. Edwards and B. Worswick, $0{\cdot}633\times10^{-15}$ sq. cm. E. Mack estimated the average **radius** of the ammonia molecule to be $1{\cdot}43\times10^{-8}$ cm.; and the average **sectional area,** $6{\cdot}40\times10^{-16}$ cm. H. G. Grimm gave $0{\cdot}94\times10^{-8}$ cm. for the radius. R. Gaus discussed the structure of the molecules of the gas. G. A. Hagemann studied what he called the contraction energy of the admixture of a mol of ammonia with 50 mols of water; but, according to R. Broom, the dilution of conc. soln. of ammonia with water is attended by an expansion, and not a contraction. J. N. Rakshit calculated the contraction on diluting aq. soln. of ammonia.

M. van Marum [2] found that the vol. of ammonia did not decrease with press. in accordance with the requirements of Boyle's law. F. Roth found that if the vol. v is unity for 0° and one atm. press., thus, at 30·2°, $p=10$, $v=0{\cdot}085$; at 46·6°, for $p=10$, 12·5, and 1·5 atm., $v=0{\cdot}095$, 0·072, and 0·059, respectively; at 52·8°, $p=15$, $v=0{\cdot}040$; and

99·6°	p	12·5	15	20	25	30	40	50	60
	v	0·076	0·063	0·046	0·036	0·029	0·021	0·015	0·010
183°	p	20	30	40	50	60	70	90	100
	v	0·049	0·032	0·023	0·018	0·014	0·012	0·010	0·009

For the relation $pv/p'v'$, H. V. Regnault gave 1·01881 when $p=703{\cdot}53$, and $p'=1435{\cdot}33$; E. P. Perman and J. H. Davies, 1·0058 for $p=0{\cdot}5$ atm., and $p'=1$ atm.; and Lord Rayleigh, 1·00632 for p between 0·5 and 1 atm. A. Lange found the **compressibility** of liquid ammonia at 13°–16·2° and 17·5 atm. to be 0·000128; at 36·3°–37·3° and 16 atm., 0·000178; and at 65°–66° and 12·5 atm., 0·000304. A Jaquerod and O. Scheuer gave for the constant a in $1-p_1v_1/P_0v_0=a(p_1-p_0)$, 0·01527 when for oxygen $a=0{\cdot}00097$. P. W. Bridgman found for the press., p, in kgrms. per sq. cm.; and the change in vol., δv, in c.c. per gram of ammonia at 30°:

p	1000	2000	3000	4000	6000	8000	10,000	12,000
δv	−0·827	−0·217	0·000	0·120	0·261	0·348	0·409	0·461

There were disturbances due to the liquefaction of the gas. F. Isambert found that the coeff. of compressibility of aq. soln. of ammonia is less than that of water alone; and the more conc. the soln., the smaller the compressibility. For a litre of liquid at 21·5° containing 330 litres of dissolved gas, the coeff. was 0·0000376, and at 20·4° with 140 litres of dissolved gas, 0·0000387. Observations were also made by G. M. Maverick, and E. L. Nichols and A. W. Wheeler. O. Maass and D. M. Morrison studied the effect of molecular attraction on the total press. of ammonia; and E. Lurie and L. J. Gillespie, the equilibrium press. of mixtures of ammonia and nitrogen. F. Schuster calculated 4512 atm. for the **internal pressure** of the liquid; and J. H. Hildebrand, 3900 atm.

H. B. Dixon and G. Greenwood found the **velocity of sound** in ammonia gas at 16·5°, 41°, and 86° to be respectively 423·4, 440·8, and 470·2 metres per sec. A. Wüllner gave 415 metres per sec. at 0°; A. Masson, 416; and G. Schwerkert, 414. N. de Kolossowsky studied the relation between the velocity of sound and the velocity of translation of the molecules. K. Dörsing gave 1663 metres per sec. for the velocity of sound in conc. aq. ammonia at 16°. J. Müller found that **diffusion** of ammonia through water increased with rise of temp. and is almost inversely as the absorption coeff. A. Fujita studied the diffusion of ammonia in various soln.; H. A. Daynes, in rubber, and J. Sameshima and K. Fukaya, the atmolysis of the gas. Y. Terada measured the rate of dialysis. O. E. Meyer and F. Springmühl found the coeff. of **viscosity** of ammonia gas to be 0·000108; or 0·511 when that of oxygen is unity. A. O. Rankine and C. J. Smith gave $\eta=0{\cdot}0_4943$ at 0° and $0{\cdot}0_31303$ at 100°, when Sutherland's constant $C=370$; T. Graham gave $0{\cdot}0_4957$ at 0°, and $0{\cdot}0_31080$ at 20°; and H. Vogel, $0{\cdot}0_4957$ at 0°, and $0{\cdot}0_4686$ at −77·1°. R. S. Edwards and B. Worswick gave 370 for Sutherland's constant. E. Thomsen measured the viscosity of binary mixtures of ammonia with hydrogen and ethylene. A. Kanitz found that the viscosity at 25° of soln. containing a gram-eq. of ammonia, NH_3, in half a litre of water is 1·0490 (water unity); in a litre, 1·0245; in 2 litres, 1·0105; in 4 litres, 1·0058; and in 8 litres, 1·0030. A. Berthoud found the **surface tension** of liquid ammonia to be 23·38° dynes per cm. at 11·10°; 18·05°, at 34·05°; and 12·95, at 58·98°. The corresponding values for the mol. **surface energy,** $\sigma(Mv)^{\frac{2}{3}}$, are 213·5, 172·25, and 127·7 ergs respectively, showing that the coeff. of association between 11° and 59° is 1·27. L. L. Grunmach gave $\sigma=41{\cdot}78$ dynes per cm. at −29°, and for the **specific cohesion,** $a^2=1{\cdot}270$ sq. mm. Observations on aq. soln. were made by H. Stocker. According to J. Domke, the surface tension, σ dynes per cm., and the sp. cohesion, a^2 sq. mm., of aq. soln. of ammonia at 18° are:

NH_4OH	0	5	10	15	20	25 per cent.
σ	73·0	66·5	63·5	61·3	59·3	87·7
a^2	14·89	13·85	13·51	13·26	13·07	12·93

P. A. Guye and L. Friedrich calculated the constants in the **equation of state**: $(p+av^{-2})(v-b)=RT$, to be $a=0{\cdot}00810$–$0{\cdot}00830$, and $b=0{\cdot}00162$–$0{\cdot}00165$ in terms of the initial vol., or $a=0{\cdot}0_5401$–$0{\cdot}0_5411$, and $b=36{\cdot}7$ per mol, or $a=138{\cdot}6$–$141{\cdot}7$, and $b=2{\cdot}11$–$2{\cdot}16$ per gram. O. Knoblauch and co-workers proposed an equation of state with three constants; F. G. Keyes suggested $p=4{\cdot}877T(v-\delta)^{-1}-34610{\cdot}1(v+1{\cdot}173)^{-2}$, where $\log_{10}\delta=0{\cdot}98130-3{\cdot}08/v$. This equation was found by P. W. Bridgman to be fundamentally incompetent to represent his observations at high press. The equations of state of ammonia vapour have been studied by G. Wobsa, and M. F. Carroll. The form and structure of the ammonia molecule was discussed by F. Hund, G. Hettner, and P. W. Bridgman.

According to E. P. Perman and J. H. Davies, a gram of ammonia at −20° occupies 1·19575 litres; at 0°, 1·2973 litres; at 50°, 1·5473 litres; and at 100°, 1·7964 litres. Hence, the coeff. of **thermal expansion** at constant press. between 0° and −20° is 0·003914; 0° and 50°, 0·003854; and between 0° and 100°, 0·003847. The press. coeff. of ammonia at constant vol. between 0° and −20° was found by E. P. Perman and J. H. Davies to be 0·004003; and between 0° and 98°, 0·003802. A. Lange found the mean coeff. of expansion for liquid ammonia represented in Table XVII; and E. C. McKelvy and C. S. Taylor, 0·00007 for the mean coeff. of expansion of the solid at −185°. W. Herz discussed the relation between the internal press. and the thermal expansion. A. Winkelmann[3] found the **thermal conductivity** of ammonia gas at 100° to be 0·0000709 cal. per cm. per second per degree, and at 0°, 0·0000458; and A. Eucken gave 0·00005135 at 0° (air=0·0000566 at 0°); 0·00004410 at −36·1°; and 0·00003820 at −57·6°. C. H. Lees found the conductivity of a 25 per cent. soln. at 18° to be 0·00109. The Joule-Thomson effect has been measured by G. Wobsa, who found that the decrease in the value of the constant with increasing press. at constant temp. indicates that the compressed vapour is in the ideal state. The results were discussed by G. A. Goodenough and W. E. Mosher, and the anomalous result by G. Wobsa is attributed to the presence of 0·5–0·7 per cent. of water in the ammonia employed in the work. The **specific heat** of ammonia gas at constant press. referred to an equal weight of water was found by H. V. Regnault[4] to be $c_p=0{\cdot}512$ between 24° and 216°; F. Haber gave 0·605 at 309°; 0·65 at 422°; and 0·69 at 523°; and W. Nernst, 0·65 at 365° to 680°. E. Wiedemann gave c_p at 0°, 0·5009; at 100°, 0·5317; and at 200°, 0·5629. For the **molecular heat** at 20°, F. Keutel gave $C_p=8{\cdot}56$, and $C_v=6{\cdot}50$; K. Schöler, at 20°, $C_p=8{\cdot}86$, and $C_v=6{\cdot}80$; G. Schweikert, at 0°, $C_p=8{\cdot}85$, and $C_v=6{\cdot}77$; J. R. Partington and H. J. Cant, at 14·5°, $C_p=8{\cdot}77$, and $C_v=6{\cdot}70$; F. Voller, $C_v=6{\cdot}6$; H. B. Dixon and G. Greenwood gave:

	16·5°	41°	63·5°	86°
C_p/C_v	1·3144	1·3095	1·3062	1·3021
C_p-C_v	20·062	2·045	2·034	2·025
C_v	6·56	6·61	6·64	6·70

and W. Nernst gave $C_p=8{\cdot}62+0{\cdot}002T+0{\cdot}0_672T^{13}$, for $p=1$ atm.; and $C_v=0{\cdot}35116+0{\cdot}0001055T+0{\cdot}0_765T^{12}$. S. W. Saunders added that the published values for the mol. ht. of ammonia gas are not very concordant, particularly at high temp., $C_v=6{\cdot}65$ at 15°; 5·55 at −4·4°; and 16·5 at −80°, where the high value is supposed to be due to polymerization. F. Haber gave from ordinary temp. up to 1000° K., $C_p=8{\cdot}04+0{\cdot}00035T+0{\cdot}0000017T^2$. W. Nernst's values are rather lower, and H. Budde's results at high temp. are 16 per cent. lower than those of F. Haber. A. Wüllner gave for the sp. ht. at constant vol., 0·38026 at 0°, and 0·41635 at 100°

The ratio of the two sp. hts. was $\gamma=1\cdot3172$ at 0°, and 1·2770 at 100°; G. Schweikert gave 1·30 at 20°; A. Masson, 1·315 at 0°; A. Cazin, 1·324 at room temp.; F. Keutel, 1·317; P. A. Müller, 1·26 at 21° to 40°; J. R. Partington and H. J. Cant, 1·308 at 14·5°; and K. Schöler found 1·30 at 0·5 atm. press. and 1·41 at 3·5 atm. press. W. G. Shilling gave:

T° K.	0°	100°	200°	400°	600°	800°	1000°
C_p	8·69	8·75	9·65	10·72	11·92	13·22	14·65
C_v	6·60	6·69	7·64	8·73	9·93	11·23	12·66
γ	1·315	1·315	1·262	1·228	1·200	1·177	1·157

He also gave $C_v=6\cdot650+0\cdot00465\theta+0\cdot0_5135\theta^2$, or $C_v=5\cdot482+0\cdot00391T+0\cdot0_5135T^2$; and $C_p=8\cdot686+0\cdot00452\theta+0\cdot0_5144\theta^2$, or $C_p=7\cdot561+0\cdot00373T+0\cdot0_5144T^2$. F. A. Giacomini gave $C_v=5\cdot55$ cals. for ammonia at −44°. N. S. Osborne and co-workers measured the sp. ht. of superheated ammonia vapour between −15° and 150°, and between 0·5 and 20 atm. press. The results can be represented by the empirical equation $C_p=1\cdot1255+0\cdot00238T+76\cdot8T^{-1}+5\cdot45p10^8T^{-4}+p(6\cdot5+3\cdot8p)10^{27}T^{-12}+2\cdot37p^6 10^{42}T^{-20}$, where C_p is expressed in joules per gram at 1°; p in metres of mercury at 0° and standard gravity; and T in the temp. on the absolute scale. C. S. Cragoe determined the sp. ht. of the sat. liquid, and of the sat. vapour. Observations on the sp. ht. of liquid ammonia were made by H. von Strombeck, L. A. Elleau and W. D. Ennis, C. Lüdeking and J. E. Starr, F. K. Keyes and H. A. Babcock, C. Dieterici and H. Drewes, A. J. Wood, and F. G. Keyes and R. B. Brownlee. The sp. ht. of liquid ammonia under saturation conditions was represented by N. S. Osborne and M. S. van Dusen, by $c=0\cdot7498-0\cdot000136\theta+4\cdot0263(133-\theta)^{\frac{1}{2}}$ cals. between −45° and 45°. The observed results are indicated in Table XX. H. A. Babcock gave 1·168 at 30°; 1·222 at 50°; 1·297 at 70°; 1·431 at 90°; and 1·538 at 100°. J. Dewar gave for the sp. ht. of solid ammonia 0·5, and for the mol. ht., 8·5. E. Donath gave 8·25 at −94·5°. M. S. Wrewsky and A. I. Kaigorodoff studied the thermal capacity of aq. soln. of ammonia at different temp.; E. F. Mueller and C. H. Meyers, the **entropy**; and C. S. Cragoe, the **Joule-Thomson effect.**

In 1799, M. van Marum[5] tried the effect of press. on ammonia, and found that drops of liquid ammonia were produced at 3 atm. press. A. F. de Fourcroy and L. N. Vauquelin subjected ammonia to a low temp., and claimed to have liquefied the gas at −40°. L. B. Guyton de Morveau also cooled the gas to −43·25° and obtained liquid ammonia. In all these cases, it is doubtful if the gas was dried sufficiently to justify the inference that the drops of liquid formed on the surface of the containing vessels were really those of liquid ammonia. M. Faraday heated silver amminochloride in one leg of a sealed Λ-tube, and cooled the other leg by immersion in a freezing mixture. He thus obtained colourless, transparent, liquid ammonia; and, in 1845, by means of a mixture of solid carbon dioxide and ether, he also

TABLE XX.—SPECIFIC HEAT OF LIQUID AMMONIA UNDER SATURATION CONDITIONS (Calories at 20° per gram. per °C.).

θ° C.	0°	1°	2°	3°	4°	5°	6°	7°	8°	9°
−40°	1·062	1·061	1·060	1·059	1·058	1·058	1·057	1·056	1·055	1·055
−30°	1·070	1·069	1·068	1·067	1·066	1·065	1·064	1·064	1·063	1·062
−20°	1·078	1·077	1·076	1·075	1·074	1·074	1·073	1·072	1·071	1·070
−10°	1·088	1·087	1·086	1·085	1·084	1·083	1·082	1·081	1·080	1·079
− 0°	1·099	1·098	1·097	1·096	1·094	1·093	1·092	1·091	1·090	1·089
+ 0°	1·099	1·100	1·101	1·103	1·104	1·105	1·106	1·108	1·109	1·110
+10°	1·112	1·113	1·114	1·116	1·117	1·118	1·120	1·122	1·123	1·125
+20°	1·126	1·128	1·129	1·131	1·132	1·134	1·136	1·137	1·139	1·141
+30°	1·142	1·146	1·146	1·148	1·150	1·152	1·154	1·156	1·158	1·160
+40°	1·162	1·164	1·166	1·169	1·171	1·173	1·176	1·178	1·181	1·183

obtained ammonia as a white, translucent, crystalline solid. The gas was also liquefied by A. Bussy. Various apparatus for the liquefaction were described by M. Faraday, R. Bunsen, L. B. Guyton de Morveau, A. Loir and C. Drion, C. G. Müller, F. P. E. Carré, C. Tellier and co-workers, S. Kern, A. Stock, etc. When ammonia gas is liquefied, heat is liberated ; and conversely, heat is absorbed when the liquid is vaporized. If liquid ammonia be evaporated, a relatively large amount of heat is absorbed from its surroundings. Advantage is taken of this fact in the preparation of artificial ice, cold storage, etc. F. P. E. Carré's *appareil propre à produire du froid* is a time-honoured application of the principle. A refrigerating plant is illustrated diagrammatically in Fig. 28. Ammonia gas is liquefied by compression in the condensing coils by means of a pump ; the heat generated as the gas liquefies is conducted away by the cold water flowing over the *condensing coils*, Fig. 28. The liquid ammonia runs into coils of pipes—*expansion coils*—dipping in brine. The press. is removed from the liquid ammonia in the expansion coils, and the heat absorbed by the rapidly evaporating liquid cools the brine below zero. The gas from the evaporating liquid is pumped back into the condensing coils ; and so the process is continuous. Cans of water placed in the brine are frozen into cakes. In cold storage rooms, the cold brine circulates in coils near the ceiling of the room to be cooled, and returns to the cooling-tank. Just as the steam engine or heat engine is an apparatus which can do work by means of the heat which is supplied to it at a high temp. and withdrawn at a low temp., the freezing machine can be regarded as a heat engine working backwards, for, by means of work, heat is withdrawn from a cold to a hotter body. In the evaporation coils of Carré's machine, the ammonia is heated and the coils are cooled ; the gas evolved is condensed in the condensing coils. There is here a fall of temp. *Absorption* takes place at a high temp., and *emission* at a lower temp. The properties of ammonia relating to refrigerating systems were discussed by W. H. Motz, S. A. Woolner, etc.

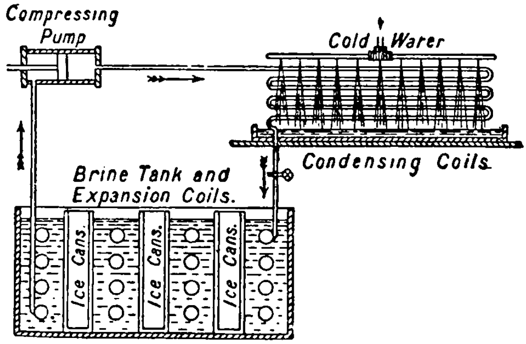

FIG. 28.—Refrigeration Plant (Diagrammatic).

According to H. Debray, between 1860–70, H. V. Regnault measured the physical constants of liquid ammonia, but the results were lost during the 1870 Franco-Prussian war. H. Debray waxes indignant :

> La main bruitale d'un soldat ennemi avait detruit, dans son laboratoire de Sèvres, les nombreux et précieux instruments de mésure qui lui avaient coute tant de labeurs et sans lequels toute recherche lui devenait impossible.

Observations on the **vapour pressure,** p mm., of liquid ammonia were made by M. Faraday, R. Bunsen, A. Blümcke, G. A. Goodenough and W. E. Mosher, H. D. Gibbs, G. Holst, R. Pictet, A. Stock and co-workers, B. Leinweber, and E. P. Perman and J. H. Davies. H. V. Regnault represented his results by the formula $\log p = 11{\cdot}504330 - 7{\cdot}4503520\alpha^{\theta+22} - 0{\cdot}9449674\beta^{\theta+22}$, where $\log \alpha = 9{\cdot}9996014 - 10$, and $\log \beta = 9{\cdot}0030729 - 10$. O. Brill found for the vap. press., p mm., of liquid ammonia :

	−79°	−70·4°	−60·8°	−50·7°	−39·8°	−33·0°
p .	38·0	74·9	212·2	309·3	568·2	761·0 mm.

and measurements by F. G. Keyes and R. B. Brownlee gave :

	−33·32°	0°	25°	50°	75°	100°	125°	132·9°
p .	760·8	3255·5	7574	15292	27857	46934	74708	(85351·8) mm.

and they represented the vap. press. between the f.p., —77°, and the critical temp., 132·9°, by the equation $\log_{10} p=-196·65T^{-1}+16·19758-0·0423858T+0·0_4 54131T^2-0·0_7 32715T^3$ mm. G. A. Burrell and I. W. Robertson represented the results by $\log p=-1951·7T^{-1}+-1·75 \log T-0·0155T+10·606$; and $\log_{10} p=-1371·86T^{-1}+8·64$; F. A. Henglein, $\log p=7·5030-2013·1T^{-1·1085}$ (p in mm.); F. Henning and co-workers, $\log p=-139360T^{-1}+1·75 \log T-0·0057034T+5·89654$; and A. Eucken and E. Karwat, $\log p=-1790·00T^{-1}-1·81630 \log T+14·97593$, for solid ammonia. R. Lorenz studied some relations of the vap. press. to other physical properties. F. Friedrichs made some observations on this subject. C. S. Cragoe and co-workers represented their results by $\log_{10} p=12·465400-1648·6068T^{-1}-0·01638646T+0·0_4 2403267T^2-0·0_7 1168708T^3$; and their data, expressed in atm. (1 atm.=760 mm. of mercury), are given in Table XXI. C. Antoine represented the vap. press. p at $\theta°$ by $\log p=1·4565\{5·4159-1000(\theta+213)\}$. V. Kirejeff discussed what he called the cohesive press. of ammonia. A. Naumann and A. Rücker observed no proportionality between the vap. press. of aq. soln., and the conc., for the partial press. decreases more rapidly than corresponds with the decrease in conc. E. P. Perman represented the relation between the partial press. of the two components—for ammonia, p, and for water, p—and the conc., x—represents the fractional number of mols. of ammonia in the liquid mixture—by $dp/dp=p_1(1-x)/px$; and this was found to co-relate the measurements fairly well. The relation between the partial press. of the water vapour and the temp., θ, was found to be $\log p=1·942+0·021950\theta-0·0000575\theta^2$ for 20 per cent. soln., and $\log p=2·051+0·0199\theta$ for 22·5 per cent. soln. A selection from the data shows:

TABLE XXI.—VAPOUR PRESSURE OF AMMONIA.

θ° C.	0°	1°	2°	3°	4°	5°	6°	7°	8°	9°
−80	0·0495	—	—	—	—	—	—	—	—	—
−70	0·1078	0·1001	0·0929	0·0861	0·0797	0·0738	0·0683	0·0631	0·0582	0·0537
−60	0·2161	0·2022	0·1891	0·1767	0·1651	0·1541	0·1437	0·1339	0·1246	0·1159
−50	0·4034	0·3800	0·3578	0·3367	0·3167	0·2977	0·2796	0·2624	0·2461	0·2307
−40	0·7083	0·6712	0·6357	0·6017	0·5693	0·5383	0·5087	0·4805	0·4536	0·4279
−30	1·1799	1·1236	1·0695	1·0175	0·9676	0·9197	0·8738	0·8297	0·7875	0·7471
−20	1·8774	1·7956	1·7166	1·6405	1·5671	1·4963	1·4281	1·3624	1·2992	1·2384
−10	2·8703	2·7555	2·6443	2·5368	2·4328	2·3322	2·2349	2·1408	2·0499	1·9621
− 0	4·2380	4·0818	3·9303	3·7832	3·6405	3·5020	3·3677	3·2375	3·1112	2·9888
+ 0	4·2380	4·3985	4·5640	4·7340	4·9090	5·0895	5·2750	5·4655	5·6610	5·8620
10	6·0685	6·2805	6·4985	6·7225	6·9520	7·1875	7·4290	7·6770	7·9310	8·1915
20	8·4585	8·7320	9·0125	9·3000	9·5940	9·8955	10·2040	10·5195	10·8430	11·1735
30	11·512	11·858	12·212	12·574	12·943	13·321	13·708	14·103	14·507	14·919
40	15·339	15·770	16·209	16·656	17·113	17·580	18·056	18·542	19·038	19·543
50	20·059	20·585	21·121	21·667	22·224	22·793	23·372	23·962	24·562	25·174
60	25·797	26·432	27·079	27·737	28·407	29·089	29·784	30·491	31·211	31·942
70	32·687	—	—	—	—	—	—	—	—	—

	0°		19·9°		40°		60°		
NH_3	9·15	19·62	10·15	19·14	11·06	20·85	3·86	11·31	per cent.
p_1 .	2·48	82·5	80·6	215·6	218·5	576·1	136·9	475·8	
p .	5·3	3·0	15·1	12·3	49·1	37·8	144·1	130·4	

A. Mittasch and co-workers measured the vap. press. of aq. soln. of ammonia, and found for p_{NH_3} mm.:

	0·3°	10·7°	20·45°	30·1°	40·0°	50·45°	60·2°
NH_3 20·70 per cent. .	101	172·5	272·5	389	614	918·5	1285·5
	0·3°	11·3°	21·3°	30·25°	39·6°	49·3°	59·3°
NH_3 29·90 per cent. .	216	354	577	815	1172	1629	2296
	0·5°	6·3°	11·0°	21·55°	30·85°		
NH_3 40·75 per cent. .	525·5	684	823	1195	1701		
	0·9°	7·1°	10·65°				
NH_3 50·83 per cent. .	1001	1330	1566				

For H. Mollier's results, *vide infra*, on the solubility of ammonia. The influence of the presence of neutral salts on the vap. press. was investigated by W. Gaus, E. P. Perman, D. P. Konowaloff, and H. Riesenfeld. The rate of escape of ammonia from aq. soln. when air is aspirated at a uniform rate through the liquid was represented by E. P. Perman by $\log q=a+bt$, where q represents the amount of ammonia in the soln. at the time t; and a and b are constants—*vide infra*. D. P. Konowaloff also made observations on this subject. A. Stock and E. Pohland, and H. Reiblen and K. T. Nestle used liquid ammonia in the tensimetric determination of mol. wts. For the vap. press. of aq. soln. of ammonia, *vide infra*. A. T. Larson and C. A. Black found that the conc. of ammonia by vol. in a compressed mixture of hydrogen and nitrogen over liquid ammonia increases with increasing temp. from —22·5° to 10°, and decreasing press. from 1000 to 50 atm. There is a definite equilibrium, and the values for ammonia are greater than those calculated from the vap. press. of liquid ammonia.

R. Bunsen calculated the **boiling point** of liquid ammonia to be —33·7° at 749·3 mm. press.; M. Faraday gave about —40° at 760 mm.; F. W. Bergstrom, —33·41°; A. Loir and C. Drion, —35·7° at 760 mm.; H. V. Regnault, —38·5° at 752 mm.; R. Pictet, —33°; R. de Forcrand, —32·5°; M. W. Travers, —38·5°; A. Joannis, —38·2° at 764 mm. press.; E. P. Perman and J. H. Davies, —33·1° at 760 mm.; and F. G. Keyes and R. B. Brownlee, —33·20° ± 0·05° at 760 mm. H. D. Gibbs gave for the b.p. of liquid ammonia at different press., p, and —33·46°

p .	293	421	557	712	867	1098	1393	1726	2146	2617 mm.
B.p. .	—50°	—45°	—40°	—35°	—30°	—25°	—20°	—15°	—10°	—5°

for the b.p. at 760 mm. N. de Kolossowsky gave 0·34–0·39 for the **ebulliscopic constant.** E. C. Franklin and C. A. Kraus found that the **molecular rise of the boiling point** of liquid ammonia is $k=0{\cdot}02T^2/\lambda$ between 3·36 and 3·44—a result which is smaller than that with any other known solvent; and L. D. Elliott gave 9·7 for the **molecular lowering of the freezing point** with soln. having 0·006–0·04 mol per 100 grms. of ammonia. L. Schmid and B. Becker gave 13·18 for the f.p. constant. H. Reiblen and K. T. Nestle made observations on this subject. T. J. Webb measured the f.p. of soln. of potassium iodide, and sodium nitrate in liquid ammonia and found evidence of a little ionization. For the **melting point,** M. Faraday gave —75°; A. Ladenburg and C. Krügel, —77·05°; A. Eucken and E. Karwat, —77·5°; L. D. Elliott, —77·73° ± 0·03°; F. G. Keyes and co-workers, —77·80: and O. Brill, and E. C. McKelvy and C. S. Taylor, —77·7°. E. C. McKelvy and C. S. Taylor gave for the **triple point** constants $\theta=-77{\cdot}70°$, 44·9 mm., and $v_1=1{\cdot}363$ c.c. per gram; and $v_s=1{\cdot}224$ c.c. per gram; and vap. press., $p=45{\cdot}2$ mm. F. W. Bergstrom gave $\theta=77{\cdot}9$ and 45·5 mm. J. Timmermans also measured the f.p. of liquid ammonia. The change of temp. of freezing per atm. change of press., given by E. C. McKelvy and C. S. Taylor, is $dT=T(v_i-V_s)dp/L$, where L, the latent heat of fusion, is 108 cals. per gram, or 0·006° per atm. The small decrease instead of increase in the temp. of the f.p. is possibly due to the presence of a trace of moisture in the gas. The **latent heat of vaporization** given by H. von Strombeck was 296·5 cals. per gram; E. C. Franklin and C. A. Kraus gave 330 cals.; H. V. Regnault, 294·5 cals. at 12°; D. S. Jacobus, 290 cals. at 12°; G. Holst, 296 cals. at 12°; T. Estreicher and A. A. Schnerr, 321·27 cals. at —33·4°; D. L. Hammick, 323 cals.; and O. Brill, 321 cals. per gram. A. Eucken and co-workers gave 7120 cals. per mol. E. Donath gave 8·25 Cals. per mol at —94·5°; 8·37 Cals. per mol at —59·3°; 5999 cals. at —74·5°; and 5705 cals. at —43·9°. For solid ammonia, A. Eucken and E. Donath gave 7499 cals. at —104°, and 7440 cals. at —85°. Results for liquid ammonia were also reported by F. G. Keyes and R. B. Brownlee, C. Ledoux, H. Mollier, V. Wood, G. A. Zeuner, C. Dieterici, G. Wobsa, C. H. Peabody, H. J. Macintire, J. Hýbl, C. E. Lucke, E. Marks, G. Holst, E. Ariès, and G. A. Goodenough and W. E. Mosher; those by N. S. Osborne and M. S. van Dusen, expressed in calories per gram, are indicated in Table XXII; and the observations are sum-

TABLE XXII.—LATENT HEAT OF VAPORIZATION OF LIQUID AMMONIA.

θ° C.	0°	1°	2°	3°	4°	5°	6°	7°	8°	9°
−40°	331·7	332·3	333·0	333·6	334·3	334·9	335·5	336·2	336·8	337·5
−30°	324·8	325·5	326·2	326·9	327·6	328·3	329·0	329·7	330·3	331·0
−20°	317·6	318·3	319·1	319·8	320·6	321·3	322·0	322·7	323·4	324·1
−10°	309·9	310·7	311·5	312·2	313·0	313·8	314·6	315·3	316·1	316·8
− 0°	301·8	302·6	303·4	304·3	305·1	305·9	306·7	307·5	308·3	309·1
+ 0°	301·8	300·9	300·1	299·2	298·4	297·5	296·6	295·7	294·9	294·0
+10°	293·1	292·2	291·3	290·4	289·5	288·6	287·6	286·7	285·7	284·8
+20°	283·8	282·8	281·8	280·9	279·9	278·9	277·9	276·9	275·9	274·9
+30°	273·9	272·8	271·8	270·7	269·7	268·6	267·5	266·4	265·3	264·2
+40°	263·1	262·0	260·8	259·7	258·5	257·4	256·2	255·0	253·8	252·6

marized in the formula $L=32{\cdot}968\sqrt{133-\theta}-0{\cdot}5895(133-\theta)$ cals. per gram. H. Mollier computed the heat of vaporization of aq. soln. of ammonia in Table XXIII, expressed in terms of calories per kilogram of the mixed vapour. This subject was also discussed by E. P. Perman. J. H. Shaxby studied the relation between the density, temp., and latent heat of vaporization; N. de Kolossowsky, the relation between the thermal expansion and the heat of vaporization; and W. Herz, the relation between the density and latent heat of vaporization. A. de Hemptinne applied M. Prud'homme's formula $L=KT(T_c-T)/(T_c-T_b)$, where T_c denotes the critical temp.; T_b, the b.p.; T, the temp. at which the latent heat L is observed. O. Brill gave 22·7 for **Trouton's constant**; and

TABLE XXIII.—HEATS OF VAPORIZATION OF AQUEOUS SOLUTION OF AMMONIA.

Temp.	Per cent. of ammonia.						
	0	11·80	23·39	33·73	41·55	50·36	100
20°	588	—	—	—	382	354	286
30°	583	—	—	394	371	353	272
40°	578	516	451	400	372	358	257
50°	572	496	428	385	369	345	—
60°	565	456	405	381	350	309	—
70°	558	480	431	405	358	—	—
80°	551	490	429	388	—	—	—
90°	544	470	424	378	—	—	—
100°	536	464	420	—	—	—	—
110°	529	478	420	—	—	—	—
120°	522	461	—	—	—	—	—

A. A. Schnerr, 22·75. R. de Forcrand, and G. Massol gave 108·1 cals. per gram for the **heat of fusion**, which is not far removed from that of water. A. Eucken and E. Karwat gave 1426 cals. per mol for the heat of fusion between 189·1° K. and 198·1° K. E. C. Franklin and C. A. Kraus have pointed out that the sp. ht. and the heat of fusion of the solid are greater than the corresponding constants for water; while the heat of volatilization, and the critical temp. and press. are higher than for any other liquid excepting water. The **molecular association** factor is as great as that of **intermolecular attraction** of ammonia. The subject was studied by E. E. Walker.

J. Dewar gave for the **critical temperature** of ammonia, 130°, and 115·0 atm. for the **critical pressure**; C. Vincent and J. Chappius gave 131·0° and 110·3 atm.; M. Centnerszwer, 132·35°; A. A. Schnerr, 132·2°; A. Jaquerod, 132·4°. F. E. C. Scheffer, 132·8° and 111·3 atm.; A. Berthoud, 132·5°–132·6° and 112 atm.; and E. Cardoso and A. Giltay, 132·90 ± 0·10°, and 112·30 atm. ± 0·10 atm. The critical opalescence was observed from 132·6° to 132·9°, with a maximum at about 132·75°. The subject was studied by W. Herz. F. G. Keyes and R. B. Brownlee gave 4·236 c.c. per gram for the **critical volume.** A. Berthoud gave for the **critical density,** 0·2362–0·2364; S. F. Pickering gave for the best representative values, T_c=405·5° K.; p_c=112 atm.; and D_c=0·236. J. A. Muller estimated the degree of polymerization in the critical state to be 1·543. The densities of ammonia, liquid and vapour, at different temp. approximate to the curve shown in Fig. 29—*vide supra*, Fig. 27; and the equation for the **mean diameter** is $\frac{1}{2}(D_v+D_1)=0{\cdot}23355+0{\cdot}0_36956(133-\theta)-0{\cdot}0_629(133-\theta)^2$. W. Herz examined the relations between the critical constants.

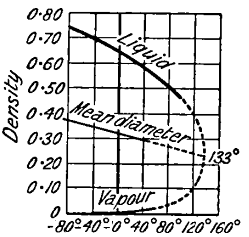

FIG. 29.—Density Curves of Ammonia — Liquid and Vapour.

B. H. Wilsdon [6] studied the energy involved in the electronic shifts during the dissociation of ammonia. J. Thomsen gave for the **heat of formation** of ammonia (N,3H)=11·89 Cals.; F. Haber, 10·95 Cals.; and M. Berthelot, 12·20 Cals. The subject was studied by R. de Forcrand. J. Thomsen gave (N,3H,Aq.)=20·3 Cals., and M. Berthelot, 21·0 Cals. A. T. Larson and R. L. Dodge calculated the following molar heats of formation from $Q_p=4{\cdot}5707(\log p_1-\log p_2)(T_1^{-1}-T_2^{-1})^{-1}$ calories:

Temp.	1	10	30	50	100 atm. press.
325°–350° . .	12,425	12,206	—	—	—
350°–375° . .	12,505	12,248	12,636	12,924	—
375°–400° . .	12,590	11,779	12,283	12,386	13,373
400°–425° . .	12,672	12.712	12,694	12,468	12,311
425°–450° . .	12,751	13,340	12,342	12,099	12,376
450°–475° . .	12,825	10,558	11,785	12,741	12,339
475°–500° . .	12,896	13,903	13,138	12,801	12,888

For the heat of combustion, J. Thomsen gave 90·65 Cals., and M. Berthelot, 91·3 Cals. The values deduced by M. de K. Thompsen for the **free energy** of ammonia at 18°, namely 45,200 cals. and 5100 cals., are incompatible—the former is based on E. Baur's observation of the e.m.f. of the cell $Pt+H_2 | NH_4NO_3$ solid, soln. of NH_4NO_3 in $NH_3 | Pt+N_2$; and the latter, on F. Haber and G. van Oordt's data for the equilibrium constant K, in $[NH_3]K=[N_2]^{\frac{1}{2}}[H_2]^{1\frac{1}{2}}$. M. Wrewsky and N. N. Sawaritzky studied the heat of formation of aq. soln. of ammonia. R. de Forcrand and G. Massol gave for the **heat of solution** of liquid ammonia, 1·882 Cals.; and G. Massol, for solid ammonia, —0·068 Cal. P. A. Favre and J. T. Silbermann gave for the heat of soln. of a mol. of ammonia in 250–370 mols. of water 8·740 Cals.; J. Thomsen, 8·440 Cals.; and M. Berthelot, 8·820 Cals. There is thus a considerable amount of heat evolved during the soln. of the gas. If a rapid current of air be driven through a cold soln. of ammonia in water, the heat absorbed as the ammonia is expelled from the soln. will reduce the temp. so as to freeze a small globule of mercury. The production of cold is best demonstrated by blowing air through a soln. of ammonia standing on a few drops of water on a block of wood. The beaker will soon be frozen to the block of wood. H. Mollier represented the heat of soln., Q, of ammonia at 15° in aq. soln. with x per cent. of ammonia, by $Q=193-1{\cdot}95x-0{\cdot}022x^2$ for values of x between 0 and 55 per cent. ammonia. Hence, $Q=0$ when $x=59{\cdot}3$. H. Mollier found for the liquid at 13°, and the gas at 15°:

x .	0	5	10	20	30	40	50	60 to 100 per cent.
Q gas	193	183	171	144	113	79	39	0 Cals.
Q liq.	493	483	471	444	413	379	339	300 Cals.

The **heat of dilution** of an aq. soln. of ammonia increases inversely as the proportion of water already in soln. increases. M. Berthelot gave the formula $Q=1270/n$

cals., for the heat of dilution, Q, in passing at 14° from $NH_3.nH_2O$ to $NH_3.200H_2O$. Thus, for $NH_3.0{\cdot}98H_2O$, the heat of dilution is 1285 cals., and for $NH_3.5{\cdot}77H_2O$, 210 cals. If Q be used to denote the heat developed per gram of ammonia when a soln. with x per cent. of ammonia is diluted to one with 0·47 per cent., H. Mollier gave $Q=79{\cdot}2x/(100-x)$. H. von Strombeck represented the amount of heat, Q, produced by the absorption of w grms. of ammonia by $Q=505{\cdot}3w$ Cals. P. Chappius gave a table of the amounts of heat developed by dissolving ammonia in water. F. Rühlemann studied the heat of soln. of ammonia in water and in alcohol. J. Thomsen gave for the heat of dilution of $NH_3.nH_2O$ to $NH_3(n+m)H_2O$ at 18°–19°, for $n=3{\cdot}2$, and $m=15$, 25, and 50, the values 324, 350, and 380 cals. respectively. W. Timoféeff found the mol. heat of soln. of 0·17–9·94 per cent. of ammonia in methyl alcohol to be 8·13–15·08 Cals.; 0·30–4·23 per cent. in ethyl alcohol, 7·03–12·30 cals.; 0·26–3·12 per cent. in propyl alcohol, 6·42–14·05 Cals.; and 0·20–3·81 per cent. in *iso*butyl alcohol, 6·04–14·40 per cent. F. E. C. Scheffer and H. J. de Wijs studied the thermodynamic potential of ammonia in soln. W. Nernst gave 3·3 for the **chemical constant** of ammonia; F. A. Henglein, and A. Langen, 2·454; S. W. Saunders, 3·4. W. Herz discussed this subject. A. Eucken and co-workers gave —1 415 for the integration constant of the thermodynamic vap. press. equation; and A. Eucken and F. Fried, 0·02 for the constant in the equilibrium equation for $3H_2+N_2=2NH_3$. A. E. van Arkel and J. H. de Boer discussed the **electronic structure** of ammonia.

The **index of refraction** of ammonia gas was measured by J. B. Biot and F. J. Arago,[7] who found 1·000381 for white light; L. Bleekrode, 1·000373; and P. L. Dulong, 1·000383. E. Mascart gave 1·000377 for the *D*-line; L. Lorenz, 0·000371; G. W. Walker, 1·000379; and E. W. Cheney gave $1{\cdot}0_33795$ for $\lambda=5852$ A.; $1{\cdot}0_33785$ for $\lambda=1{\cdot}0_33785$; and $1{\cdot}0_33771$ for $\lambda=6678$ A. C. and M. Cuthbertson found for

λ . . .	480	520·9	546·1	643·8	$670{\cdot}8\mu\mu$
μ . . .	$1{\cdot}0_338300$	$1{\cdot}0_338002$	$1{\cdot}0_337860$	$1{\cdot}0_337455$	$1{\cdot}0_337376$

S. Loria and J. Patkowsky made observations between $\lambda=435{\cdot}8\mu\mu$ and $382{\cdot}5\mu\mu$. The constants for the formula $\mu-1=C/(n_0{}^2-n^2)$ are $C'=2{\cdot}9658\times10^{27}$, and $n_0{}^2=8135{\cdot}3\times10^{27}$ for C. and M. Cuthbertson's data; and $C=2{\cdot}7898\times10^{27}$, and $n_0{}^2=7509{\cdot}8\times10^{27}$ for S. Loria and J. Patkowsky's data, C. S. Cragoe and co-workers obtained 0·0003831 at 0° and 760 mm. for the yellow He-line $\mu=1{\cdot}0016927$ at —0·33°; 1·0011592 at —10·55°; 0·0003080 at —40·67°; and 0·0001884 at —49·93°. L. Bleekrode obtained 1·325 for the index of refraction of liquid ammonia. S. Friberg obtained values for the index of refraction and dispersion in the ultra-violet. R. Lorenz and W. Herz compared the mol. refraction and the mol. vol. with those of other substances. G. Szivessy found **Kerr's constant** to be $0{\cdot}59\times10^{-10}$ at 17·9°; and C. V. Raman and K. S. Krishnan, $0{\cdot}59\times10^{-10}$ at 20° and atm. press., with the *D*-line. C. P. Smyth studied the refraction of the H_2N: radicles. K. R. Ramanathan and N. G. Srinivasan found the depolarization of light scattered by ammonia in a direction perpendicular to the incident beam is the same as it is with hydrogen chloride or sulphide. This indicates a high degree of optical symmetry. This is taken to mean that in these gases electrons of the hydrogen atoms have gone to the outer orbits of the heavier atoms to complete the electronic structure characteristic of the nearest inert gas. S. C. Lind and co-workers studied the decomposition of ammonia by α-**rays.** H. B. Wahlin examined the effect of free electrons on ammonia molecules.

A. Schuster [8] found that the **spectrum** of ammonia in the discharge tube shows a broad, greenish-yellow band between 5688 and 5627. G. Magnanini observed the spectrum of the flame of ammonia burning in oxygen exhibits a large number of hydrogen lines. This spectrum was also observed by J. M. Eder, who measured 240 lines between $\lambda=5000$ and 2262 for the extreme ultra-violet. The emission spectrum has seven characteristic bands—one between the red and ultra-violet, and the other six are in the ultra-violet. L. de Boisbaudran, D. M. Dennison, B. Hasselberg, G. Landsberg and A. Predwoditeleff, H. C. Dibbits, W. B. Rimmer, H. O. Kneser, B. J. Spense, F. Holweck, H. Deslandres, W. H. Bair, O. Reinkober, G. Hettner, H. Leupold, C. T. Kwei, K. Schierkolk, and K. B. Hofmann, observed this spectrum. The band $\lambda=3360$ observed by J. M. Eder has been studied by E. P. Lewis, who found it occurred with mixtures of hydrogen and nitrogen in vacuum tubes; and by A. Fowler and C. C. L. Gregory, who found it also occurred in the solar spectrum. The absorption of heat rays by ammonia gas was examined by J. Tyndall, G. A. Stinchcomb and E. F. Barker, P. M. Garibaldi, L. Schönn, W. J. Russell and W. Lapraik, W. de W. Abney and E. R. Festing, and W. W. Coblentz; and the absorption of ultra-violet rays, by W. N. Hartley and J. J. Dobbie, M. Ferrières, W. B. Rimmer, S. W. Leifson, and J. L. Soret. W. W. Coblentz studied the ultra-red absorption spectrum of ammonia, and found bands near 3·0μ, 6·0μ, and from 7·8μ to 15μ. K. Schierkolk resolved the last of these into a double band, and he found strong bands at 1·493μ and 1·935μ, with a weaker one at 1·643μ. There was also a strong band at 2·22μ, with two sharp maxima at 2·202μ and 2·239μ. W. F. Colby and E. F. Barker studied this subject; and B. J. Spense examined the spectrum in the vicinity of 3μ. G. Landsberg and A. Predwoditeleff studied the absorption spectrum of ammonia; and K. Glen, and E. Hulthèn and S. Nakamura, the origin of the bands. The absorption of ultra-violet rays by liquid ammonia was studied by L. Ciechomsky; and the absorption spectrum of ammonia-water, by J. L. Soret. W. N. Hartley and J. J. Dobbie attributed the band from $\lambda=2707$ to $\lambda=2322$ in commercial aq. ammonia to organic impurities.

According to M. Ascoli,[9] liquid ammonia shows the phenomenon of **electrosmose.** When a difference of potential is established between two portions of liquid ammonia separated by a porous septum of calcined alumina, and kept at a temp. of —60° by immersion in a bath of acetone cooled with solid carbon dioxide, there is usually a slight displacement of the liquid in the opposite direction to the current; but if the liquid is coloured blue by the formation of a small quantity of sodammonium in soln. there is a marked displacement of the liquid in the same direction as the current, showing that the introduction of the sodium has caused the liquid to become positively and the alumina negatively electrified.

The **electrical conductivity** of liquid ammonia is very small, and the passage of the current is accompanied by the evolution of a little gas. L. Bleekrode said that it is a good conductor; but K. T. Kemp, and J. W. Hittorf suggested that the observed conductivity of the liquid is really an effect of the presence of impurities—mainly water. C. Frenzel found the sp. conductivity of liquid ammonia of a high degree of purity to be $0{\cdot}0_{6}133$ mho at —79·3°, and $0{\cdot}0_{6}147$ mho at —73·6°, with a temp. coeff. of about 1·9 per cent. per degree. H. M. Goodwin and M. de K. Thompson obtained a sp. conductivity of $0{\cdot}0_{3}1392$ mho at —29·5°; $0{\cdot}0_{3}1485$ mho at —20°; and of $0{\cdot}0_{3}1688$ mho at —13°. The mean temp. coeff. between —30° and —12° is $dK/d\theta=0{\cdot}0_{5}11$, the increase being at the rate of about 0·7 per cent. per degree rise of temp. This is unusually small. N. Tchitchinadzé, and E. C. Franklin and C. A. Kraus also studied this subject. C. Frenzel attributed the conductivity of liquid ammonia to ionization $NH_3 \rightleftharpoons NH'_2 + H^{\cdot} \rightleftharpoons NH'' + 2H^{\cdot} \rightleftharpoons N''' + 3H^{\cdot}$, because in the curve showing the relation between the quantity and intensity of current, there are three breaks, Fig. 30. He also believed that some of the $H^{\cdot}$-ions unite with the ammonia molecules, forming $NH^{\cdot}_4$-ions. H. P. Cady showed that the mol. conductivity of salts dissolved in liquid ammonia, at its b.p. —34°, is generally greater than is the case in aq. soln. at 18°, e.g. the mol. conductivity of a soln. of potassium nitrate in liquid ammonia is 124, and in water 114 ($v=100$); potassium bromide in ammonia ($v=135$) is 181, and in water ($v=128$), only 117; silver nitrate in

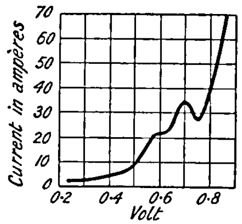

Fig. 30.—Amperage-Voltage Curves of Liquid Ammoniacal Solutions.

ammonia ($v=140$) is 147, and only 103·3 in water at a greater dilution ($v=166$). Mercuric iodide is but slightly ionized in aq. soln., but in ammonia soln. ($v=150$) the mol. conductivity is 102. H. M. Goodwin and M. de K. Thompson measured the conductivity of silver nitrate in ammonia soln. E. C. Franklin and co-workers, F. A. Smith, and P. Eversheim have examined the conductivities of many salts, etc., dissolved in liquid ammonia.

W. Hisinger and J. J. Berzelius found that the electrolysis of a conc. aq. soln. of ammonia with iron electrodes results in the evolution of hydrogen at the cathode, and nitrogen at the anode; if the soln. be less conc., oxygen may also be developed, and iron oxide formed. J. J. Berzelius and M. M. Pontin made ammonium amalgam (*q.v.*) with mercury as the negative cathode, and aq. ammonia at the anode where, during the electrolysis, oxygen was evolved. A highly purified aq. soln. of ammonia is almost as bad a conductor as purified water. M. Faraday showed that if a little ammonium sulphate be added, the aq. soln. on electrolysis furnishes between 3 and 4 vols. of hydrogen at the cathode per vol. of nitrogen at the anode. S. M. Losanitsch and M. Z. Jovitschitsch attribute the deficiency in the anodic nitrogen to the formation of nitrites in soln. F. Kohlrausch found that only when in dil. soln. does aq. ammonia behave like a normal electrolyte; and W. Ostwald represented the relation between the conductivity and the conc. of the soln. by $\tan \mu=(v/v_0)^{0\cdot4124}$, where μ represents the conductivity; v_0, the dilution—in litres per mol—at which the mol. conductivity has half its maximum value; and v, the dilution in litres per mol. The conductivity has been measured by G. Bredig, F. Kohlrausch, F. Goldschmidt, etc. G. Bredig found for the sp. conductivity, in mho, of N-soln.:

N . .	0·0109	0·0553	0·3148	0·953	2·955	4·720	12·89
Mho . .	$0{\cdot}0_31220$	$0{\cdot}0_32788$	$0{\cdot}0_36339$	0·001002	0·001296	0·001218	$0{\cdot}0_34323$

thus showing that with increasing conc., the sp. conductivity first rises to a maximum nearly 0·0013 for $3N$-soln., and then steadily falls as illustrated by Fig. 31. One of the factors concerned in the reversal of the conductivity is attributed by F. Goldschmidt to the effect of ammonia on the viscosity of the soln. observed by A. Kanitz, and the decreased mobility of the ions. Aq. soln. of salts which exert no chemical action on the ammonia have their conductivity lowered by additions of ammonia.

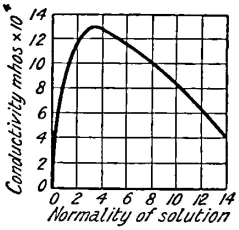

FIG. 31.—Specific Electrical Conductivity of Aqueous Solutions of Ammonia.

When ammonia is dissolved in water the deviation from Henry's law has been attributed to a chemical reaction between water and ammonia, forming *ammonium hydroxide*: $NH_3+H_2O \rightleftharpoons NH_4OH$; this inference is supported by the great difference, 3·4 Cals., between the heat of soln., 8·4 Cals., and the heat of condensation, 5·0 Cals. The 3·4 Cals. here represent the heat of admixture of a mol of ammonia with water, and this is much greater than the heat of admixture of ammonia with other liquids which do not react chemically with the ammonia. There is also a possibility that *ammonia hydrates*, $NH_3.nH_2O$, are formed, *vide infra*; and a possibility that the ammonium hydroxide is ionized $NH_4OH \rightleftharpoons NH^{\cdot}_4+OH'$. In agreement with the assumption that ammonium hydroxide is formed which acts as a weak base, the liquid tastes alkaline; it reddens turmeric; colours the juice of violets green; and colours litmus, etc., the same as do soln. of the alkali hydroxides. These changes of colour disappear on exposure to air owing to the volatilization of the ammonia—the volatile alkali of the early chemists. The feeble character of ammonium hydroxide as a base is evidenced by its heat of neutralization with acids which is about 1·5 Cals. less than is the case with potassium or sodium hydroxides; like other weak bases, the soln. cannot be satisfactorily titrated with phenolphthalein; S. Arrhenius found that its effect on the hydrolysis of ethyl acetate is about 40 times less than that of sodium hydroxide; and the electrical conductivity of aq. soln. of ammonia is small. The hydrolysis of ammonium salts was discussed by C. Brück, and E. Baars. L. Knorr explained the interaction of ammonia and ethylene oxide not as an effect of the addition of $NH^{\cdot}_4$ and OH'-ions usually assumed to be present in aq. soln., but apparently to the addition of $H^{\cdot}$ and NH'_2 or of $H^{\cdot}$ and $NH_3OH.'$ The conc. of the $H^{\cdot}$-ions in the soln. of ammonia cannot be greater than in water, owing to the presence of OH'-ions, hence, it is assumed that NH'_2 or NH_3OH'-ions are present in the soln. in addition to OH' and $NH^{\cdot}_4$-ions. B. Cassen found that Maxwell's distribution law does not hold for the motions of lithium ions in liquid ammonia.

F. Goldschmidt found that the **ionization constant,** K, varies from $0{\cdot}0_4221$ to $0{\cdot}0_623$ for $0{\cdot}0109N$- to $12{\cdot}89N$-soln. As the conc. of the soln. decreases, the value of K becomes nearly constant, as, assuming this begins with a conc. of $0{\cdot}02N$, K is 0·0000191. E. Klarmann gave 0·0000152. The inconstancy of K cannot be attributed to the formation of complex ions—*e.g.* $NH_4(NH_3)^{\cdot}$—since the lowering of the f.p. of water containing ammonia and ammonium salts corresponds with the value calculated for the quantity of material added. F. Goldschmidt found the increase in the partial press. of ammonia is almost exactly proportional to the amount of carbamide added to the soln. and the value of k calculated from $(k+[H_2O])\lambda'^2p=(k+[H^2O]')\lambda^2p'$ is negative and nearly constant. Here $[H_2O]$ denotes the active mass of water taken as 100, and $[H_2O]'$ the active mass of water after the addition of carbamide; λ and λ' are the eq. conductivities; p, p', the partial press. of ammonia of the soln. with and without the carbamide; and k represents the hydration constant. The variation of the active mass of the water is proportional to the variation of the vap. press. on the assumption that only a monohydroxide is formed. W. M. Burke measured the conductivities of soln. of ammonia at various conc. in $2M$-carbamide at 25°, and found that the ionization, as in aq. soln., conforms with the law of mass action, but the ionization constant is $12{\cdot}92\times10^{-6}$ in carbamide soln. as against $18{\cdot}1\times10^{-6}$ in aq. soln., thus presenting an exception to J. J. Thomson's hypothesis—**1.** 9, 8. The 30 per cent. difference cannot be due entirely, or to any large extent, to a change in viscosity, and it is possible that an ammonium-carbamide complex is formed which has a smaller ionization constant than ammonium hydroxide. M. Mizutani studied soln. of ammonia in water and alcohol.

A. Hantzsch and J. Sebaldt argued that if in aq. soln. ammonia exists as hydroxide, the scheme of ionization is $NH_3+H_2O\rightleftharpoons NH_4OH\rightleftharpoons NH^{\cdot}_4+OH'$, and assuming that the hydroxide is insoluble in chloroform, the conc. of ammonia, NH_3, in the aq. phase is proportional to that of the hydroxide, and the total conc. may be used in calculating the partition ratio of ammonia between water and chloroform. The partition coeff. between water and chloroform is 25 at 25°, and remains constant for varying conc., but the value changes with temp., so that at 2° the partition coeff. is 38·53. The higher the temp. the greater the proportion of ammonia in the chloroform. This is taken to mean that the ammonia is hydrated in aq. soln. forming not NH_4OH, but a complex $NH_3{\cdot}nH_2O$. R. Abegg and H. Riesenfeld measured the partial press. of ammonia in soln. of various salts, and found for conc. $0{\cdot}5$–$1{\cdot}0N$, at 25°, the partial press. was proportional to the conc. In almost all cases the addition of an alkali salt causes an increase of the partial press. of ammonia, this increase being proportional to the conc. of the salt; lithium salts are, however, exceptional. The salts may be divided into two groups, those giving a mol. increase of press. less than 2·3 and those giving a mol. increase greater than 3·4. Those giving the lower value are those containing univalent anions. The following, however, gave the higher value: hydroxides, fluorides, borates, acetates, formates, chlorates, and iodates, the action being apparently additive. The higher value appears to be connected with the tendency to form hydrates, whilst hydrates do not exist in the case of the salts for which the lower value is obtained. H. Riesenfeld compared the results at 25°, and found the only soln. for which a marked temp. coeff. exists are those of sodium and potassium carbonates, sodium and lithium chlorides. In these cases, presumably, there is interaction between the ammonia and the dissolved salt. For sodium hydroxide, potassium hydroxide, chloride, nitrate, acetate, and oxalate, the temp. coeff. is practically zero. It appears from the observations that where there is interaction between ammonia and the dissolved salt, it is greater for sodium than for potassium salts, and greater for lithium than for sodium salts. D. I. Konowaloff worked at 60°. W. Gaus worked at 23° and 27°. He found that sodium hydroxide and most ammonium salts caused, as expected, an increase of press., sodium and potassium chlorides also causing an increase. Ammonium nitrate, iodide, and thiocyanate, however, bring about a decrease of press., the cause of which may be due to the formation of complex compounds. All the other salts examined produced a decrease, which was most marked in the case of cupric and silver salts. G. S. Forbes and C. E. Norton measured the oxidation potentials of a number of organic ammonium radicles and of the alkali metals in liquid ammonia; and A. A. Groening and H. P. Cady, the decomposition potentials and metal overvoltages of soln. of salts in liquid ammonia. L. B. Loeb investigated the mobilities of ions in mixtures of ammonia and air or hydrogen.

According to G. Bredig, the velocity of migration of the $NH_4^{\cdot}$-ion at 25° is 70·4; and, according to F. Kohlrausch, 64 at 18°. The eq. conductivity $\lambda_0=271$. Assuming that $NH_4^{\cdot}$ and OH' are the only ions present in aq. soln., about 4 per cent. of a 0·01N-soln. is ionized, in a 0·1N-soln., over 1 per cent.; and in a N-soln., about 0·35 per cent. F. W. Bergstrom found the electrochemical series in liquid ammonia is Pb, Bi, Sn, Sb, As, P, Te, Se, S, I. H. P. Cady studied **concentration cells** with soln. of sodium nitrate in liquid ammonia, using sodium amalgam electrodes, and found that the laws valid for aq. soln. also apply to ammonia soln. E. Baur studied the e.m.f. of the **gas cell** with electrodes of platinum charged with hydrogen and nitrogen, and a soln. of ammonium nitrate sat. with ammonia, or a sat. aq. soln. of ammonia. The most constant results were obtained with the former liquid. At —10°, the e.m.f. is 0·59 volt. The e.m.f. falls rapidly when current is drawn from the cell, but the normal value is regained on standing, indicating that the current is produced by the union of hydrogen and nitrogen to form ammonia. He also measured the decomposition tension of the two electrolytes. G. S. Forbes and C. E. Norton measured the oxidation potentials of quaternary ammonium radicles and of alkali metals in liquid ammonia. W. Wild studied the **electrocapillary action** of soln. of potassium chloride and nitrate, mercuric nitrate, and nitric acid in liquid ammonia. A. T. Waldie obtained a critical ionizing potential at 11 volts, and possibly one at 33 volts. G. Gehlhoff studied the fall in the cathode potential by a constant discharge in a vacuum tube; L. B. Loeb and co-workers, G. C. Grindley and A. M. Tyndall, and A. T. Waldie, the mobilities of the ions in ammonia gas; and W. G. Palmer, the effect of ammonia gas on the coherer in detecting electric waves.

C. A. Mackay gave 11·1 volts for the **ionizing potential** of the gas; R. A. Morton and R. W. Riding, 11·7 volts; and A. T. Waldie, 11 volts. H. Henstock discussed the electronic structure; and L. B. Loeb, L. B. Loeb and M. F. Ashley, and H. R. Hasse, the mobilities of ions in gaseous mixtures of air and ammonia. H. M. Goodwin and M. de K. Thompson[10] found the **dielectric constant** of commercial liquid ammonia at —34° to be 21; ammonia prepared from ammonium chloride and lime, 23; and commercial liquid ammonia after dehydration, 22. C. T. Zahn found the dielectric constant, ϵ, to be:

	−71·3°	1·4°	23·7°	98·4°	183·9°
$(\epsilon-1)\times10^6$ . .	9280	7132	6117	4018	2734

He did not observe an anomaly indicated by M. Jona at room temp., but there is a definite increase near the point of liquefaction. The results can be represented by P. Debye's expression $(\epsilon-1)vT=0·000768T+1·74$, where v denotes the sp. vol. of 1 c.c. of an ideal gas at n.p. θ. C. Manneback also studied the dielectric capacity of ammonia. G. Jung discussed the orientation of the molecules in dielectric fluids; L. Ebert, the dielectric polarization; and A. Tschukareff, the magnetochemical effect in the reaction $NH_3+HCl=NH_4Cl$. K. Wolf found a discontinuity in the dielectric constant-pressure curve of ammonia when traces of moisture are present.

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§ 17. The Solubility of Ammonia

Ammonia is rapidly and copiously dissolved by water; and much heat is developed. Ice also dissolves ammonia rapidly and at the same time liquefies with a reduction of temp. The rapid solubility in water has been the subject of some pretty experiments for the lecture table.[1] According to H. Davy,[2] water dissolves about half its weight of ammonia gas, or nearly 670 times its vol. at 10° and 29·8 ins. press.; and at a lower temp., J. Dalton said that water dissolves more than half its own weight of gas. Observations were also made by T. Thomson, and A. Ure. More accurate measurements were made by L. Carius, O. Wachsmuth, T. K. Sherwood, E. M. Baker, F. M. Raoult, J. W. Doyer, H. Watts, W. Gaus, E. P. Perman, and R. Abegg and H. Riesenfeld. H. E. Roscoe and W. Dittmar gave for the solubility, S, expressed in grams of ammonia per 100 grms. of water, at 760 mm.:

	0°	5°	10°	15°	20°	25°	30°	40°	50°	56°
S . .	87·5	77·5	67·9	60·0	52·6	46·0	40·3	30·7	22·9	18·5

while T. H. Sims obtained rather higher values, at 760 mm.:

	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	96°
S . .	89·9	68·4	51·8	40·8	33·8	28·4	23·8	19·4	15·4	11·4	7·4

L. Carius represented his results by $S=1049{\cdot}624-29{\cdot}4963\theta+0{\cdot}676874\theta^2-0{\cdot}0095621\theta^3$. J. W. Mallet obtained for low temp., and a press. of 743·5 mm.:

	−3·9°	−10°	−20°	−25°	−30°	−40°
S . .	94·7	111·5	176·8	255·4	278·1	294·6

The ice-curve was examined by F. Rüdorff, F. Guthrie, and S. U. Pickering; and the equilibrium curves of the binary system, by L. D. Elliot, S. Postma, F. F. Rupert, and A. Smits and S. Postma, who found:

NH_3	0	20	35	50	57·5	60	66·6	75	78	90	100 per cent.
F.p.	0°	−32°	−120°	−77°	−89°	−85·5°	−78°	−80°	−95°	−83°	−77°

$$\underbrace{0^\circ\ -32^\circ\ -120^\circ}_{\text{Ice}} \rightleftharpoons \underbrace{-120^\circ\ -77^\circ\ -89^\circ}_{NH_3.H_2O} \rightleftharpoons \underbrace{-89^\circ\ -85{\cdot}5^\circ\ -78^\circ\ -80^\circ\ -95^\circ}_{NH_3.\frac{1}{2}H_2O} \rightleftharpoons \underbrace{-95^\circ\ -83^\circ\ -77^\circ}_{NH_3}$$

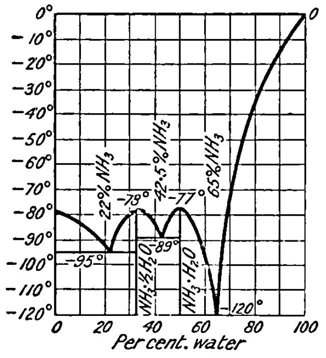

FIG. 32.—Equilibrium with the Binary System NH_3–H_2O.

The results are plotted in Fig. 32. There are thus two hydrates, **ammonia hydrate**, $NH_3.H_2O$, or **ammonium hydroxide**, NH_4OH, which forms small, colourless crystals melting at −77°. F. F. Rupert gave −79° for the m.p., and L. D. Elliot, −78·9°, and **ammonia hemihydrate**, $NH_3.\frac{1}{2}H_2O$, which forms needle-shaped crystals melting at −78°: F. F. Rupert gave −79° for the m.p., and L. D. Elliot, −79·2°. F. Friedrichs questioned the existence of these hydrates and suggested that they may be a case of mixed crystals in a continuous series. This is an *argumentum contra factum*. E. Baud and L. Gay observed maxima in curves, representing (i) the variation of the heats of dilution of ammonia with different proportions of water, and (ii) the contraction attending the dilution of ammonia with water; these maxima corresponded with the existence of a hemihydrate and a monohydrate. F. Friedrichs, W. H. Motz, G. Baume and A. Tykociner, and A. M. Wasilieff also studied the system. According to F. F. Rupert, the eutectic between NH_3 and $NH_3 \cdot \frac{1}{2}H_2O$ lies at $-94°$ with 80·3 per cent. of NH_3; and that between $NH_3 \cdot \frac{1}{2}H_2O$ and $NH_3.H_2O$, at $-87°$ and 57·3 per cent. NH_3. The effect of press. on the solubility of ammonia in water was examined by H. E. Roscoe and W. Dittmar, at 0°, and press. between 10 mm. and 2000 mm. The following are selected from T. H. Sims' results at 0°, where S denotes the number of grams of ammonia dissolved in a gram of water at the given press., p, the partial press., *i.e.* the total press. less the press. of the aq. vapour at the given temp.; and C, the number of grams of ammonia that would have been present in a gram of water if the solubility were proportional to the press.

p . .	20	100	250	500	750	1000	1500	1900
S . .	0·082	0·280	0·472	0·692	0·891	1·126	1·656	2·070
C . .	3·113	2·127	1·434	1·052	0·903	0·855	0·839	0·823

This shows that the solubility of ammonia in water is not described by Henry's law; but at 100°, the solubility data are in accord with the law:

p . .	750	800	900	1000	1100	1200	1300	1400
S . .	0·068	0·078	0·088	0·096	0·106	0·115	0·125	0·135
C . .	0·074	0·074	0·074	0·073	0·073	0·073	0·073	0·073

D. P. Konowaloff also showed that the law, invalid at ordinary temp., becomes valid at 100°. G. Calingaert and F. E. Huggins observed that the apparent deviation from Henry's law does not occur if an allowance be made for the ionization of the ammonia in aq. soln.: $NH_3+H_2O \rightleftharpoons NH^{\cdot}_4+OH'$, so that only that part of the ammonia not ionized is taken as being proportional to the conc. of the ammonia in the vapour phase. The constant for Henry's ratio with sufficiently dilute soln. is unity, and such a soln. distils without variation of conc., and corresponds to a maximum boiling mixture. The conc. of such a liquid is 0·000010 grm. of ammonia per litre. For the ratio of the partial press., p mm., and the number of mols of ammonia, n, in soln., W. Gaus, and R. Abegg and H. Riesenfeld found the deviation to be small for small conc. of ammonia. J. Locke and J. Forssall represented the relation between p and n by $p=13{\cdot}34n+0{\cdot}18n^2$. E. Klarmann observed that Henry's law applies for soln. of conc. ranging from $0{\cdot}0083N$- to $0{\cdot}5N$-NH_4OH; and said that the action in aq. soln. can be represented either by $NH_3+H_2O \rightleftharpoons NH_4OH$, and $NH_4OH \rightleftharpoons NH^{\cdot}_4+OH'$; or by $NH_3+H^{\cdot}=NH^{\cdot}_4$, and $H^{\cdot}+OH'=H_2O$. F. E. C. Scheffer and H. J. de Wijs said that the equilibrium constant of $NH_{3\text{gas}} \rightleftharpoons NH_{3\text{dissolved}}$ cannot be determined, but since for $NH_3+H_2O \rightleftharpoons NH_4OH$, $K=[NH_4OH]/[NH_3]$, so that if C denotes the total conc. of the ammonia, then $[NH_3]/C=[NH_3]/([NH_3]+[NH_4OH])=(K+1)^{-1}=$constant. The equilibrium constant of $NH_{3\text{gas}}+nH_2O \rightleftharpoons \{nNH_4OH+(1-n)NH_3\}_{\text{dissolved}}$, can be determined by means of the ratio p_{NH_3}/C, where p_{NH_3} is the press. of the gas above the liquid. Henry's law holds for conc. up to $2N$-NH_3. The vap. press., p, of the ammonia can be represented by $p=12{\cdot}9C(1+0{\cdot}046C)$. The addition of a constant small quantity (0·15 mol) of ammonium nitrate to varying conc. of ammonia has no influence on the agreement of the ratio p/C with Henry's law, or the above equilibrium conditions, but the effect of additions of increasing quantities of the salt to small conc. of ammonia can be represented by $p=12{\cdot}9C(1+0{\cdot}019C_n+0{\cdot}0085C_n^2)$, where C_n denotes the conc. of the ammonium nitrate. The subject has been discussed by E. Baars in his *Ueber den Zustand des Ammoniaks in wässriger Lösung* (Stuttgart, 1927).

E. P. Perman, and H. Mollier measured the relation between the vap. press., temp., and percentage conc. of aq. soln. of ammonia. The latter's results for the percentage conc. of the soln. at different temp. and press. are shown in Table XXIV,

TABLE XXIV.—THE CONCENTRATIONS OF AQUEOUS SOLUTION OF AMMONIA AT DIFFERENT TEMPERATURES AND PRESSURES.

Press. kgrms. per sq. cm.	20°	30°	40°	50°	60°	70°	80°	90°	100°	110°	120°	130°	140°	150°
1·0	33·95	28·55	23·30	18·25	13·65	9·47	5·75	2·50	—	—	—	—	—	—
1·5	39·98	34·30	28·76	23·70	18·84	14·30	10·10	6·26	3·03	0·15	—	—	—	—
2·0	44·82	38·71	33·20	28·00	23·00	18·17	13·72	9·60	6·00	2·70	—	—	—	—
2·5	48·80	42·36	36·70	31·45	26·33	21·45	16·81	12·46	8·52	5·02	1·92	—	—	—
3·0	—	45·62	38·70	34·38	29·26	24·35	19·63	15·10	10·98	7·20	3·88	0·81	—	—
4·0	—	51·07	44·64	38·96	33·87	28·90	24·07	19·40	15·02	10·96	7·20	3·85	0·80	—
5·0	—	—	49·00	43·01	37·70	32·52	27·70	22·98	18·51	14·28	10·22	6·60	3·32	0·28
6·0	—	—	—	46·57	40·97	35·72	30·86	26·09	21·50	17·21	13·03	9·15	5·67	2·44
7·0	—	—	—	49·72	44·00	38·55	33·60	28·77	24·15	19·80	15·55	11·55	7·90	4·45
8·0	—	—	—	52·71	46·74	41·15	36·00	31·18	26·58	22·05	17·80	13·73	9·98	6·40
9·0	—	—	—	—	49·36	43·65	38·40	33·42	28·75	24·12	19·80	15·68	11·80	8·16
10·0	—	—	—	—	51·80	46·07	40·67	35·58	30·73	26·00	21·60	17·40	13·45	9·71

and the results are plotted in Fig. 33. The total press. exerted by the vapours from soln. of different conc. and temp. are shown in Table XXV, and plotted in Fig. 34. The temp. of aq. soln. of ammonia of different conc. and vap. press. are indicated in Table XXVI, and plotted in Fig. 35. B. S. Neuhausen and W. A. Patrick represented their results by $v=0{\cdot}49(p\sigma/p_0)^{0{\cdot}69}$, where v denotes the vol. occupied by the liquid gas dissolved per gram of water; p_0, the vap. press.; p, the equilibrium gas press.; and σ, the surface tension of the liquefied gas at the given temp. R. Mezger and T. Payer measured the vap. press. of mixed soln. of ammonia and carbon dioxide. R. O. E. Davis and co-workers, E. Klarmann, W. K. Lewis and W. G. Whitman, T. A. Wilson, W. C. Sproesser and G. B. Taylor, R. T. Haslam and co-workers, O. L. Kowalke and co-workers, O. A. Hougen, W. G. Whitman and D. S. Davis measured the effect of gas velocity, temp., etc., on the rate of absorption of ammonia; and

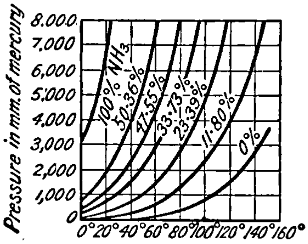

FIG. 33.—Concentration Lines for Aqueous Solutions of Ammonia at Different Temperatures.

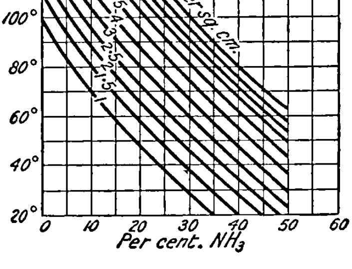

FIG. 34.—Isobaric Lines for Aqueous Solutions of Ammonia at Different Concentrations and Temperatures.

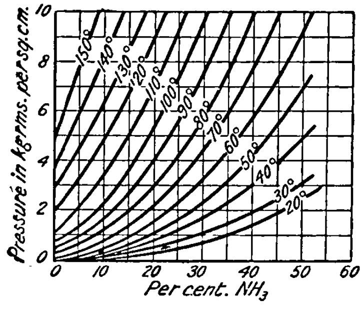

FIG. 35.—Isothermal Lines for Aqueous Solutions of Ammonia at Different Pressures and Concentrations.

P. G. Ledig, the rate of absorption from gas-bubbles. E. B. Auerbach and L. Millbradt compared the rates of escape of ammonia and water from aq. soln. They found that the loss from soln. with 34·5, 25·7, and 22·7 per cent. of ammonia was respectively 28·3, 19·4, and 16·4 per cent., while only one to two per cent. of water was lost—*vide supra.*

TABLE XXV.—THE TOTAL VAPOUR PRESSURE OF AQUEOUS SOLUTIONS OF AMMONIA AT DIFFERENT TEMPERATURES AND CONCENTRATIONS.

Conc. per cent.	20°	30°	40°	50°	60°	70°	80°	90°	100°	110°	120°	130°	140°	150°
5	—	—	—	—	—	—	—	1·32	1·83	2·49	3·33	4·40	5·71	7·28
10	—	—	—	—	—	1·05	1·48	2·07	2·80	3·73	4·92	6·35	8·01	10·20
15	—	—	—	—	1·12	1·58	2·20	2·99	3·99	5·24	6·77	8·64	—	—
20	—	—	—	1·14	1·63	2·27	3·09	4·15	5·48	7·08	9·12	—	—	—
25	—	—	1·14	1·64	2·28	3·14	4·24	5·64	7·34	9·45	—	—	—	—
30	—	1·13	1·63	2·28	3·16	4·29	5·71	7·49	9·62	—	—	—	—	—
35	1·08	1·57	2·25	3·14	4·27	5·76	7·52	9·73	—	—	—	—	—	—
40	1·50	2·17	3·07	4·24	5·70	7·55	9·70	—	—	—	—	—	—	—
45	2·02	2·91	4·08	5·55	7·36	9·56	—	—	—	—	—	—	—	—
50	2·66	3·79	5·24	7·09	9·26	—	—	—	—	—	—	—	—	—

TABLE XXVI.—THE TEMPERATURES OF AQUEOUS SOLUTIONS OF AMMONIA OF DIFFERENT CONCENTRATIONS AND PRESSURES.

Per cent.	Pressures in kilograms per sq. cm.											
	1·0	1·5	2·0	2·5	3·0	4·0	5·0	6·0	7·0	8·0	9·0	10·0
5	82·3°	93·75°	102·95°	110·05°	116·3°	126·4°	134·8°	142·0°	148·3°	153·8°	159·0°	163·6°
10	68·65	80·1	88·95	96·2	102·5	112·5	120·6	127·8	134·1	139·85	144·8	149·25
15	56·95	68·4	77·0	84·1	90·45	100·1	108·3	115·2	121·3	126·8	131·7	136·0
20	46·5	57·6	66·1	73·1	79·3	88·7	96·7	103·5	109·6	114·8	119·5	123·7
25	36·7	47·4	55·9	62·7	68·7	78·1	85·7	92·3	98·2	103·5	108·0	112·3
30	27·4	37·8	46·1	52·8	58·7	67·1	75·2	81·7	87·45	92·5	97·3	101·5
35	18·3	28·7	56·6	43·25	48·8	57·7	65·2	71·4	77·2	82·0	86·8	91·1
40	—	20·0	27·8	34·1	39·5	48·2	55·7	61·8	67·4	72·3	76·9	81·3
45	—	—	19·8	25·7	30·9	39·4	46·7	52·8	58·2	63·1	67·6	71·9
50	—	—	—	18·0	22·9	31·5	38·4	44·0	49·6	54·3	58·8	63·1

F. M. Raoult found the solubility of ammonia in a 11·25 per cent. soln. of *potassium hydroxide* to be at 0°, 8°, and 24° respectively, 72·0, 57·0, and 37·3 per cent.; and in a 25·25 per cent. soln., 49·5, 37·5, and 21·8 per cent. The solubility results with soln. of *sodium hydroxide* were the same as with potassium hydroxide, R. Abegg and H. Riesenfeld found that a litre of $\frac{1}{2}N$-, N-, and $1\frac{1}{2}$-N soln. of the potassium hydroxide at 25° dissolves respectively 0·852, 0·716, and 0·607 mol.; sodium hydroxide, 0·876, 0·789, and 0·716 mol ; and *lithium hydroxide,* 0·865, 0·808, and 0·768 mol. H. Riesenfeld made observations with potassium and sodium hydroxides at 35°. C. A. Lobry de Bruyn found that 100 grms. of a sat. soln. of *hydroxylamine* contain 26 grms. of ammonia at 0° and 19–20 grms. at 15°–16°. A. Waller said that when potassium hydroxide is dissolved in aq. ammonia, bubbles of gas are disengaged, but are reabsorbed in the upper portion of the liquid. R. Abegg and H. Riesenfeld found that at 25°, the solubilities of ammonia in mols per litre of $\frac{1}{2}N$-, N-, and $1\frac{1}{2}N$-soln. of the following salts are respectively as follow : *potassium fluoride,* 0·839, 0·722, 0·626 ; *potassium chloride,* 0·930, 0·866, 0·809 ; *sodium chloride,* 0·938, 0·889, 0·843 ; and *lithium chloride,* 0·980, 1·008, 1·045. H. Riesenfeld made observations with potassium and sodium chlorides at 35°. F. M. Raoult found that a soln. of *ammonium chloride* absorbs slightly less ammonia than the same vol. of water. Continuing R. Abegg and H. Riesenfeld's observations at 25°, *potassium bromide*, 0·950, 0·904, 0·857 ; *sodium bromide*, 0·965, 0·916, 0·890 ; *lithium bromide*, 1·001, 1·040, 1·090 ; *potassium iodide*, 0·970, 0·942, 0·900 ; *sodium iodide*, 0·995, 0·992, 0·985 ; and *lithium iodide*, 1·030, 1·094, 1·190. R. O. E. Davis and co-workers sought a solvent for ammonia which would not attack metals. Soln. of ammonium nitrate were recommended by B. B. Kuriloff, and of ammonium thiocyanate were recommended by H. W. Foote and M. A. Hunter; of the salts tested, *lithium nitrate* alone forms a liquid with ammonia in the absence of water, whilst *calcium nitrate* tetrahydrate liquefies in the presence of a little water. The ammonia contained in 1 c.c. of the lithium nitrate soln. sat. at 24° is eq. to 26·0 c.c. of 0·95*N*-sulphuric acid, whilst that for the calcium nitrate soln. under identical conditions is 18·5 c.c. of 0·95*N*-acid. Vap. press. measurements have been made for the soln. 36·34 per cent. ammonia, 63·66 per cent. lithium nitrate, and for several other mixtures containing 6·06–58·66 per cent. of water. The soln. of ammonia in lithium nitrate have no action on machine steel, iron wire, and nichrome wire after several months' contact, but nickel steel shows a slight action after several months. The results show that a soln. of lithium nitrate in ammonia with a small percentage of water should be a good absorbent for the removal of ammonia from mixtures of nitrogen, hydrogen, and ammonia. The absorption could be effected at 0°, and a large proportion of the ammonia released either by a small increase of temp. or by reduction of the press. D. P. Konowaloff found that the solubility of ammonia in soln. of *sodium nitrate, ammonium nitrate,* and *silver diamminonitrate* is nearly the same as in water alone. Continuing R. Abegg and H. Riesenfeld's observations, *potassium nitrate* gave 0·923, 0·862, and 0·804 ; and *potassium nitrite*, 0·920, 0·855, 0·798. F. M. Raoult showed that a soln. of sodium nitrate or *ammonium nitrate* absorbs nearly the same amount of ammonia as the same vol. of water. For a 28·38 per cent. soln. of *calcium nitrate*, F. M. Raoult gave for the solubility at 0°, 8°, and 16° respectively 96·25, 78·50, and 65·00 per cent. of ammonia ; and for a 59·03 per cent. soln. of that salt, 104·5, 84·75, and 70·5 per cent. H. Riesenfeld made observations on the solubility of ammonia in soln. of *sodium and potassium carbonates* at 35° ; and R. Abegg and H. Riesenfeld, with the soln. and units previously employed obtained for potassium carbonate, 0·788, 0·650, and 0·554. G. S. Newth, and B. S. Proctor noticed two distinct liquids are formed when conc. aq. ammonia and a sat. soln. of *potassium carbonate* are mixed, and allowed to stand. With soln. sat. at ordinary temp., the lower liquid dissolves about 37 per cent. by vol. of ammonia, and the upper liquid about 6 per cent. of the potassium carbonate soln. Working with an aq. soln. of ammonia of sp. gr. 0·885, and a soln. of potassium carbonate sat. at 25°, the solubility curve of potassium carbonate in aq. ammonia is represented by *AC*, Fig. 36, and that of ammonia in the potassium carbonate soln., by *CB*. The curves meet at 43°, so that above that critical soln. temp. the liquids are miscible in all proportions. The curves with 10 per cent. of water by vol. are shown at A_1, C_1, B_1, and the critical soln. temp. is now 25° ; and with 12·9 and 18·1 per cent. of added water, the critical soln. temp. is respectively $C_2=10°$, and $C_3=0°$. H. Riesenfeld measured the solubility of ammonia in soln. of *potassium acetate*, and *potassium oxalate* at 35°. R. Abegg and H. Riesenfeld found that at 25° the solubility of ammonia in ½*N*-, *N*-, and 1·5*N*-soln., expressed in mol of ammonia per litre, was for potassium oxalate, 0·866, 0·771, 0·675 ; potassium acetate, 0·866, 0·765, 0·685 ; *potassium formate*, 0·868, 0·760, 0·678 ; *potassium cyanide*, 0·926, 0·858, 0·802 ; *potassium thiocyanate*, 0·932, 0·868, 0·814 ; *sodium sulphide*, 0·887, 0·795, 0·726 ; *potassium sulphite*, 0·865, 0·768, 0·675 ; *potassium sulphate*, 0·875, 0·772, 0·678 ; *potassium chromate*, 0·866, 0·771, 0·675 ; *potassium borate*, 0·814, 0·677, 0·560 ; *potassium*

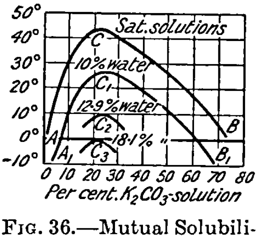

FIG. 36.—Mutual Solubilities of Aqueous Solutions of Potassium Carbonate and Ammonia.

hydrophosphate, 0·860, 0·749, 0·664 ; and for $\frac{1}{4}N$-soln. of *potassium chlorate*, 0·927 mol NH_3 ; *potassium bromate*, 0·940 ; and *potassium iodate*, 0·951. According to E. Weitz, ammonium salts of monobasic acids are in general more soluble in ammonia than in water alone ; those of polybasic acids are less soluble, and may be salted out of soln. by passing in ammonia gas. The difference is attributed to the formation of soluble ammonia additive compounds by monobasic salts, but not by polybasic salts. Fluoride, iodate, periodate, and borate behave as if the acids were polybasic, probably owing to polymerization. On the other hand, the persulphate and the dithionate show the same effect as monobasic salts, possibly because the substituted hydrogen atoms are in two distinct branches of the structural mol.

P. F. G. Boullay gave 33·3 parts for the solubility of ammonia in 100 parts of alcohol at 38° ; J. Müller said that one vol. of absolute alcohol dissolves 340 vols. of ammonia at 20° and 760 mm. ; and S. Pagliano and A. Emo said that ammonia is much less soluble in ethyl, propyl, or amyl alcohol than it is in water. C. A. Lobry de Bruyn represented the solubility of ammonia in absolute *methyl alcohol*, expressed in grams per 100 grms. of soln., by

		0°	5°	10°	15°	20°	25°	30°
S	CH_3OH . .	29·3	26·5	24·2	21·6	19·2	16·5	14·0
	C_2H_5OH . .	19·7	17·5	15·0	13·2	11·5	10·0	8·8

His results for absolute *ethyl alcohol* are also indicated. B. S. Neuhausen also studied the solubility of ammonia in methyl and ethyl alcohols. S. M. Delépine obtained values for ethyl alcohol about 4 per cent. higher ; and he measured the sp. gr. and the solubility of soln. of ammonia in aq. soln. of ethyl alcohol. Thus, he obtained :

	C_2H_5OH . .	96	90	80	60	50 per cent.
S	at 0° . .	24·5	30·25	39·0	50·45	69·77
	at 30° . .	10·7	11·4	12·2	21·2	25·25

Vide supra, for the heats of soln. of ammonia in methyl, ethyl, propyl, and isobutyl alcohols. W. Herz and H. Fischer measured the distribution of ammonia between *amyl alcohol* and water at 25° ; and, expressing the results in grams per 100 c.c., he found :

Aqueous layer . . .	0·5	1·0	2·0	3·0	4·0	5·0
Alcoholic layer . . .	0·072	0·147	0·272	0·438	0·595	0·756

H. M. Dawson and J. McCrae, and A. Hantzsch and J. Sebalt found for the distribution of ammonia between *chloroform* and water at 20° :

Aqueous layer .	0·2	0·4	0·6	0·8	1·0	1·2	1·4	1·6
Alcoholic layer .	0·007	0·015	0·023	0·031	0·039	0·046	0·055	0·063

H. M. Dawson and J. McCrae, D. P. Konowaloff, and W. Gaus also used soln. of various salts of the alkali metals, and of potassium, sodium, cupric, or barium hydroxide in place of water ; and also copper sulphate, copper chloride, zinc sulphate, and cadmium iodide ; while M. S. Sherrill and D. E. Russ examined the effect of ammonium chromate. W. Herz and A. Kurzer examined the distribution of ammonia between water and a mixture of amyl alcohol and chloroform. Observations on the distribution of ammonia between water and chloroform were made by T. S. Moore and T. F. Winmill, G. A. Abbott and W. C. Bray, and J. M. Bell. J. H. Hildebrand gave for the molar fraction $N \times 10^4$ of ammonia at 1 atm. press., and 25°, dissolved by ethyl alcohol, 2300 ; methyl alcohol, 2730 ; and water, 3300.

Ammonia is readily soluble in *ether ;* A. Christoff said that one vol. of ether at 760 mm. dissolves 17·13 vols. of ammonia at 0° ; 12·35 vols. at 10° ; and 10·27 vols. at 15°. N. T. de Saussure found that one vol. of *turpentine* dissolves 7·5 vols. of ammonia at 16° ; one vol. of *oil of lemon*, 8·5 vols. at 16° ; one vol. of *oil of rosemary*, 9·75 vols. at 29° ; one vol. of *oil of lavender*, 47 vols. at 20° ; and one vol. of *petroleum*, 0·4 vol. of ammonia. L. S. Kubie found that mineral oil at room temp. dissolves 0·071 c.c. of nitrogen per c.c. of oil. A. Hantzsch and A. Vogt found that the distribution of ammonia in grams per 1000 c.c. between *toluene* and air is at 0°, 0·366 and 0·0396 grm.; at 10°, 0·357 and 0·0435 grm.; at 20°, 0·326 and 0·0451 grm.; and at 30°, 0·286 and 0·0462 grm. C. Himly showed that one vol. of *caoutchouc* absorbs 3 vols. of ammonia; G. Cauquil, that a litre of *cyclohexanol* at 26° and 755 mm. press. dissolves 28166·66 c.c. of ammonia; and C. Gerhardt, that *valerol* absorbs much ammonia.

Recently heated *charcoal* was found by N. T. de Saussure[3] to absorb considerable quantities of ammonia, and J. Hunter showed that the raising of the temp. lowered the vol. of gas absorbed:

	0°	5°	10°	15°	20°	25°	30°	35°
Vols. NH_3 .	170·7	169·6	163·8	157·6	148·6	140·1	131·9	123·0

and the raising of the press. increased the vol. of gas absorbed:

p . .	760	1104·3	1178·0	1269·2	1369·5	1486·5	1795·1	2002·6	2608·5
Vols. NH_3 .	170·7	174·3	176·0	178·2	180·8	183·5	188·7	196·7	209·8

G. G. Longinescu and C. N. Theodosu, H. Franzen and O. von Meyer, P. A. Favre, P. Chappius, O. Ruff and G. Rösner, R. Chaplin, A. Magnus and C. Cahn, and E. W. R. Pfeiffer also studied the effects of temp. and press.—*vide* **5**. 39, 9—and F. G. Keyes and M. J. Marshall gave 6456 cals. per mol for the heat of absorption on charcoal. P. Chappius examined the absorption of ammonia by *asbestos* and *meerschaum;* E. H. Jenkins, by *gypsum;* L. Y. Davidheiser and W. A. Patrick, by *silica gel;* L. A. Munro and F. M. G. Johnson, by *alumina;* and N. Nikitin, by alumina, *chromic oxide*, and *ferric oxide;* D. H. Bangham and F. P. Burt, and M. Crespi and E. Moles, by *glass;* R. Seeliger, by dehydrated *chabazite;* and W. A. Dew and H. S. Taylor, by *copper*, *nickel*, and *iron*. J. D. Edwards and S. F. Pickering found that if the permeability of *rubber* to hydrogen is unity, the value for ammonia is 8·0.

In the following survey of the behaviour of different substances in liquid ammonia, the observations of G. Gore[4] are indicated by "G.," and those of E. C. Franklin and co-workers, by "F."; v.s. is put for "very soluble"; s. for "soluble"; s.s., "sparingly soluble"; n.s. for "insoluble"; and m. for "miscible." **Aluminium**: metal, n.s., G.; chloride, n.s., F.; acetate, n.s., F. **Ammonium**: acetate—L. Troost; arsenate, n.s., F.; bromide, v.s., F.; borate, s.s., F.; bromide, v.s., F.; carbonate, n.s., G. and F.; chloride, v.s., G. and F.; chromate, s.s., F.; hypophosphate, s., F.; iodide, v.s., F.; molybdate, n.s., F.; nitrate, v.s., G. and F.; orthophosphate, n.s., F.; selenate, n.s., F.; sulphate, n.s., F.; sulphide, v.s., F.; thiocyanate, v.s., F.; vanadate, n.s., G.; oxalate, n.s., F.; oxalurate, s., F.; and thionurate, s., F. H. Moissan found sulphammonium easily soluble in liquid ammonia; and E. Rengade, ammonium carbamate to be soluble. H. Stamm discussed the solubility of ammonium salts in ammonia. **Antimony**: metal n.s., G.; bromide, v.s., G.; trichloride, swells, n.s., G.; fluoride, swells, n.s., G.; iodide, reacts, G.; oxide, n.s., G.; hydrated pentoxide, s.s., G.—see A. Rosenheim and F. Jacobsohn; oxybromide, s.s., G.; oxychloride, unchanged, G.; red sulphide, n.s.; orange sulphide, s., G.; black sulphide, n.s., G.; tartrate, n.s., F.; and potassium pyroantimonate, n.s., G. **Arsenic**: metal, n.s., G. and F.; amide, n.s., C. Hugot; arsenious acid, n.s., G. and F.; potassium arsenide, n.s., C. Hugot; arsenic acid, s.s., G.—see A. Rosenheim and F. Jacobsohn; tribromide, swells, C. Hugot; trichloride, reacts, G. and F.; auripigmentum, s.s., G. and F.; and realgar, s., G. **Barium**: metal, n.s., G. A. Guntz and R. C. Mentrel; amide, n.s., R. C. Mentrel; carbonyl, n.s., R. C. Mentrel; chloride, swells, n.s., G. and F.; nitrate, v.s., G., s., F.—see F. Friedrichs; nitride, n.s., R. C. Mentrel; oxide, n.s., G.; hydroxide, n.s., G. and F.; sulphate, n.s., G. and F.; and acetate, s.s., F. **Beryllium**: carbonate, chloride, oxide, and sulphate, n.s., G. **Bismuth**: metal, n.s., G.; carbonate, n.s., G.; chloride, s., G.; oxychloride, n.s., F.; fluoride, n.s., G.; hydroxide, n.s., G.; iodide, s.s., F.; nitrate (soluble in presence of ammonium nitrate) and sulphide, n.s., G. **Boron**: element, n.s., G.; amide, s., J. A. Joannis; chloride and bromide, react; imide, n.s. A. Stock and M. Blix's, and J. A. Joannis' imide is soluble in the presence of sulphur; nitride—see A. Stock and M. Blix; oxide, n.s., G.; boric acid, s.s., F.; and sulphide, reacts, A. Stock and M. Blix. **Cadmium**: bromide, n.s., G. and F.; carbonate, n.s., G.; chloride, n.s., G. and F.; fluoride, n.s., G.; iodide, n.s., G., s.s., F.; nitrate, s., F.; sulphate, n.s., F.; and sulphide, n.s., G. and F. **Cæsium**: metal, v.s., H. Moissan; alum, n.s., F.; acetylide, s., H. Moissan; carbide—see H. Moissan; and hydride, reacts, H. Moissan. **Calcium**: metal, n.s., G., s.s., H. Moissan; amide—see H. Moissan;

bromide, s.s., F.; carbonate, n.s., F.; chloride, n.s., F. and G.; nitrate, v.s., F.; oxide, orthophosphate, sulphide, sulphite, formate, and butyrate, n.s., F.; polysulphide, n.s., H. Moissan; and acetate, s.s., F. **Carbon:** wood-charcoal, and graphite, n.s., G.; carbonyl chloride, reacts, F.; dioxide—see E. Rengade; monoxide—see J. A. Joannis; hexachloride, n.s., G.; tetrabromide, v.s., G.; tetrachloride, m., G. and F.; disulphide, reacts, G. and F.; acetylene—see H. Moissan; amylene, not miscible, G.; diisoamylene, n.s., F.; hexane, n.s., F.; paraffin, n.s., G.; benzene, s., F.; naphthalene, s.s., G. and F.; and anthracene, n.s., G. and F. **Cerium:** chloride, fluoride, and oxide, n.s., G.; and nitrate, s.s., G. and F. **Chromium:** chloride, swells, s.s., G.; fluoride, n.s., G.; chromic acid, swells, s.s., G., s.s., F.; and chrome-alum, n.s., G.—see A. Rosenheim and F. Jacobsohn. **Cobalt:** carbonate, n.s., G.; chloride, and sulphate, n.s., F. and G., swells, G.; fluoride, n.s., G.; nitrate, s., F.; and oxide, n.s., G. and F. **Columbium:** columbic acid, n.s., G. **Copper:** metal, reacts, G. and F.; ammonium chloride, s.s., F.; arsenate, and arsenite, n.s., F.; carbonate, n.s., G. and F.; chloride, swells, n.s., G., and n.s. A. Bouzat; cuprous chloride, s.s., F.; chromate, n.s., G.; cyanide, s., G.; cuprous cyanide, s., G.; ferrocyanide, n.s., G.; fluoride, n.s., G.; cuprous iodide, n.s., G.; v.s., F.; nitrate, v.s., F.—see F. Friedrichs; oxide, reacts, G. and F.; cuprous oxide, reacts, G., phosphate, n.s., G.; cryst. sulphate, n.s.; anhydrous sulphate, n.s.. swells, G., n.s., A. Bouzat; sulphide, n.s.; acetate, s.s., F.; formate, s.s., F.; and benzoate, s., J. A. Joannis. **Didymium:** nitrate, s., F. **Gold:** chloride, reacts, s.s., G. **Indium:** metal, n.s., G.; black oxide, n.s., F. **Iodine:** element, s., F. and G.—see F. Friedrichs; iodic acid, n.s., G. and F., and nitrogen iodide, n.s., C. Hugot. **Iridium:** potassium chloroiridate, osmium-iridium alloy; and iridium oxide, n.s., G. **Iron:** metal, n.s., G.; ferricbromide, s.s., F.; iodide, v.s., F.; pyrophosphate, n.s., F.; and sulphate, swells, n.s., G.; *ferrous*-potassium cyanide, no change, G., n.s., F.; sulphate, n.s., F.; sulphide, n.s., F.; lactate, s.s., F.; valerianate, s.s., F. **Lanthanum:** sulphate, n.s., G. **Lead:** metal, n.s., G.; bromide, s., F.; carbonate, n.s., F.; chloride, swells, n.s., G., s.s., F.; chromate, n.s., G. and F., dichromate, s.s., G. and F.; fluoride, n.s., G.; iodide, s.s., G., v.s, F.; nitrate, s.s., G. and F.—see F. Friedrichs; litharge, n.s., F.; red-lead, n.s., G. and F.; dioxide, n.s., F.; galena, n.s., F.; acetate, v.s., F.; formate, s., F.; and tartrate, n.s., F. **Lithium:** metal, s., G., F., and H. Moissan; amide, s.s., H. Moissan; antimonide, s., P. Lebeau; bromide, s., F.; carbonate, n.s., F.; chloride, s.s., F.; iodide, v.s., F.; methyl ammonium, s., H. Moissan; nitrate, v.s., F.; benzoate, v.s., F.; and salicylate, v.s., F. **Magnesium:** metal, n.s., G.; bromide, s.s., F.; carbonate, n.s., F.; oxychloride, s.s., F.; cyanamide, s., F.; iodide, v.s., F.; nitrate, v.s., F.; oxide, phosphate, sulphate, sulphide, and sulphite, n.s., F.; acetamide, s., F.; and benzoy-sulphamide, s., F. **Manganese:** metal, n.s., G.; bromide, and carbonate, n.s., G. and F.; chloride, n.s., G. and F.; fluoride, n.s., G.; iodide, s., F.; nitrate, v.s., F.; sulphate, n.s., G. and F. **Mercury:** metal, n.s., G.; bromide, s.s., reacts, G.; chloride, s., G. and F.; mercurous chloride, v.s., G.; cyanide, v.s., G. and F.; iodide, v.s., G. and F.; mercurous iodide, v.s., F.; nitrate, s., G. and F., reacts, G.; mercurous nitrate, v.s., G. and F.; yellow oxide, n.s., F. and G., but soluble in the presence of ammonium nitrate; red oxide, n.s., G.; mercurous oxide, n.s., F.; thiocyanate, v.s., F.; sulphate, s.s., G., n.s., F.; cinnabar, n.s., G.; fulminate, v.s., F.; and mercurous acetate, v.s., G. and F. **Molybdenum:** metal, n.s., G. and F.; molybdic acid, n.s., G. and F.; and sulphide, n.s., G.—see A. Rosenheim and F. Jacobsohn. **Nickel:** metal, n.s., G.; chloride, swells, G., n.s., G. and F.; fluoride and hydroxide, n.s., G.; nitrate, s., F.; oxide, n.s., G.; and sulphate, n.s., F. **Nitrogen:** no reaction, J. A. Joannis; nitric and nitrous oxides—see J. A. Joannis; iodide, n.s., C. Hugot. For ammonium iodide, bromide, chloride, azide, and carbonate, and hydroxylamine chloride, and hydrazine chloride—see F. Friedrichs. **Osmium:** metal, n.s., G.; osmium-iridium alloy, n.s., G.; and osmic acid, reacts, G. **Palladium:** metal, n.s., G.; chloride, s.s., G.; and sulphide, n.s., G. **Phosphorus:** red, n.s., G. and F.; white, s., G. and F; trichloride, reacts, G. and F.; pentachloride, reacts, F., v.s., G.; pentoxide, s.s., G., n.s., F.; amide—see J. A. Joannis; nitride—see A. Stock and B. Hofmann; hydride—see J. A. Joannis; phosphoric acid, no change, and pentasulphide, s., A. Stock and B. Hoffmann. **Platinum:** metal, n.s., G.; platinous chloride, s.s., G.; chloride, s.s., G.; iodide, v.s., G.; and oxide, n.s., G. **Potassium:** metal, s., G. and F.; amide, v.s., J. A. Joannis, pyroantimonate, n.s., F.; arsenide, s., C. Hugot; tetrarsenide, v.s., C. Hugot; bromide, s.s., G., s., F.; carbonate, n.s., F.; carbonyl—see J. A. Joannis; chlorate, s., F.; chloride, s.s., G. and F.; chloroiridate, n.s., F.; chromate, s.s., G., n.s., F.; dichromate, s.s., G. and F.; cyanate, v.s., F.; cyanide, n.s., G.; s., F.; ferrous cyanide, n.s., G. and F.; fluoride, s.s., G.; fluosilicate, n.s., G.; fluozirconate, n.s., G.; hydride—see H. Moissan; hydroxide, n.s., F.; hypophosphite, s.s., F.; iridate, n.s., G.; iodate, n.s., F.; iodide, s.s., G. and F.—see F. Friedrichs; nitrate, s.s., F.; nitrite, s.s., F.; oxide, dioxide, and tetroxide, n.s., F.; permanganate, v.s., G. and F.; metaphosphate, n.s., F.; pentaphosphide, v.s., C. Hugot; hydrophosphide, s.s., J. A. Joannis; thiocyanate, s., G. and F.—see F. Friedrichs; selenide, n.s., C. Hugot; tetraselenide, s., C. Hugot; sulphamide, v.s., F.; sulphate, n.s., F.; sulphide, s., F., n.s., C. Hugot; pentasulphide, s., C. Hugot; sulphite, n.s., F.; telluride, n.s., C. Hugot; trinitride—see J. A. Joannis; tritelluride, s., C. Hugot; acetate, s.s., F.; ethyl sulphate, v.s., F.; benzolsulphate, s., F.; orthonitrophenolsulphate, s., F.; nitroprusside, v.s., F.; formate—see E. Rengade; acetamide, v.s., F.; benzamide, s., F.; benzoylsulphamide, s., F.; urea, s., F.; *m*-methoxybenzoylsulphamide, s.s., F.; phenylacetamide, v.s., F.; saccharine, s., F.; and *p*-toluosulphamide, s.s., F. **Rubidium**: metal, s., G., F., and H. Moissan; acetylide, s., H. Moissan; carbide—see H. Moissan; chloride, s.s., F.; and fluoride, n.s., G. **Selenium**: no change, G., s., F.; n.s., C. Hugot; selenious acid, n.s., G.; selenic acid, n.s., F. **Silver**: metal, n.s., G.; arsenate, n.s., G.; bromide, swells, s.s., G., s., F.—see F. Friedrichs; carbonate, swells, n.s., G., n.s., F.; chloride, swells, G., s.s., F.—see F. Friedrichs; chromate, n.s., G.; cyanide, v.s., G. and F.—see F. Friedrichs; fluoride, s.s., G.; iodate, n.s., G.; iodide, v.s., G. and F.; nitrate, v.s., G. and F.—see F. Friedrichs; nitrite, v.s., F.; azide—see F. Friedrichs; oxide, swells, n.s., G.; n.s., F.; dioxide, n.s., G.; phosphate, n.s., G.; sulphate, swells, n.s., G., n.s., F.; vanadate, n.s., G.; acetate, s.s., F.; and thioethylcarbamate, n.s., F. **Silicon**: amide, n.s., E. Vigouroux and C. Hugot; disulphide, reacts, M. Blix and W. Wirbelauer; sulphochloride, reacts, M. Blix and W. Wirbelauer; sulphourea, n.s., M. Blix; tetrachloride, reacts, M. Blix and C. Hugot; crystalline silica, n.s., G.; precipitated silica, n.s., G. **Sodium**: metal, s., G. and F.; amide, and antimonide, s.s., J. A. Joannis; arsenide, s., C. Hugot; diborate, n.s., F.; lead alloy, s., J. A. Joannis; bromate, s., F.; bromide, v.s., F.—for sodium bromide, and azide, see F. Friedrichs; carbide, s., H. Moissan; carbonate, n.s., F.; carbonyl—see J. A. Joannis; chlorate, v.s., F.; chloride, s.s., G., s., F.; dichromate, s.s., F.; hydroxide, n.s., F. N. Tchitchinadzé found 2·5 mgrms. of sodium hydroxide are dissolved per 1000 grms. of liquid ammonia, or 1·8 mgrms. per litre, and the solubility is much augmented if moisture be present; hyponitrite—see J. A. Joannis; hypophosphate, s.s., F.; iodide, and nitrate, s.s.; trinitride, J. A. Joannis; nitride, v.s., F.; oxide, dioxide, and trioxide, n.s., J. A. Joannis; permanganate, s.; pyrophosphate, n.s., F.; triphosphide, v.s., C. Hugot; phosphomolybdate, n.s., F.; hydrophosphide, s., J. A. Joannis; and $Na_3H_3P_2$, s.s., C. Hugot; selenide, n.s., C. Hugot, tetraselenide, s., C. Hugot; sulphate and hydrosulphate, n.s., F.; sulphide, n.s., C. Hugot; pentasulphide, s., C. Hugot; sulphite, n.s., F.; telluride, n.s., C. Hugot; tritelluride, s., C. Hugot; thiosulphate, s., C. Hugot; bismuthide, s.s., C. Hugot; tungstate, s.s., F.; acetate, s.s., F.; formate, s.s., F.; ethylsulphate, v.s., F.; benzoylsulphinate, s., F.; carbamate, n.s., E. Rengade; citrate, n.s.; propionate, s.s., F.; salicylate, v.s., F.; valerianate, n.s., F.; and *o*-xylenesulphinate, s. **Strontium**: metal, n.s., G., s.s., A. Guntz; carbonate, n.s., F.; chloride, n.s., F.; nitrate, v.s., F.—see F. Friedrichs; and sulphate, n.s., F. **Sulphur**: element, s., G. and F.—see F. Friedrichs; chloride, s., G. and F.; iodide, v.s., F.; carbide, reacts, G. and F.; nitride, v.s., O. Ruff and E. Geisel; sulphamide, v.s., F. **Tellurium**: n.s., F., G., and C. Hugot; nitride—see R. Metzner; tetrachloride, reacts, R. Metzner. **Thallium**: metal, n.s., G. and F.; chloride, n.s., F.; fluoride, n.s., G.; nitrate, s., F.; peroxide, n.s., G. **Thorium** sulphate, n.s., G. **Tin**: metal, monoxide, and dioxide, n.s., G.; dichloride, s., G.—see F. Friedrichs; and tetrachloride, v.s., G. **Titanium**: nitrocyanide, black oxide, and dioxide, n.s., G.; and tetrachloride—see M. Blix. **Tungsten**: metal and oxide, n.s., G.—see A. Rosenheim and F. Jacobsohn. **Uranium** fluoride, s.s., G., nitrate and oxide, react, G.—see A. Rosenheim and F. Jacobsohn. **Vanadium**: nitride and oxide, n.s., G. **Zinc**: bromide, swells, n.s., G., s.s., F.; carbonate, n.s., F.; chloride, swells, n.s., G., n.s., F.; chromate, n.s., F.: cyanide, s.s., G., v.s., F.; ferrocyamide, s.s., F.; fluoride, n.s., G.; iodide, swells, n.s., G., s., F.; nitrate, s.s., F.; oxide, phosphate, sulphide, and sulphate, n.s., F.; acetate, s., F.; lactate, v.s., F.; and tartrate, n.s., F. **Zirconium**: metal, and oxide, n.s., G.; and tetrachloride—see M. Blix.

The following qualitative observations on the action of liquid ammonia on organic compounds are mainly by E. C. Franklin and C. A. Kraus, those in brackets are by G. Gore. *Aliphatic compounds.*—**Halides**: methyl iodide, m.; chloroform, reacts, and m.; bromoform, m.; iodoform, v.s., ethyl bromide and iodide, s.; ethylene bromide, s.; ethylidene chloride, m.; isobutyl bromide, s.; amyl bromide, s.s.; tribromomethane, v.s.; nitrotrichloromethane, m.; perchloroethane (n.s.); perchloroethylene (m.); dichloroacetylene (s.). **Alcohols**: methyl, m.; ethyl, m.; propyl, m.; normal butyl, m.; isobutyl, m.; tertiary butyl, m.; amyl, m.; heptyl, m.; octyl, m.; cetyl, n.s.; ethylene glycol, m.; propylene glycol, m.; glycerol, m.; erythrite, s.s.; dulcite, s.s.; and mannite, s.s. **Ethers**: diethyl other, m.; diamyl ether, s.s.; and methylal, m. **Aldehydes**: acetaldehyde, m.; paraldehyde, m.; aldehyde ammonia, s.; chloral hydrate, s.; bromal hydrate, v.s.; chloral cyanhydrate, v.s.; isobutyl aldehyde, v.s.; valeraldehyde, v.s.; heptylaldehyde, s.; glyoxal, n.s.; pinacone, v.s.; and oxymethylene, n.s. **Monobasic acids**: formic, m.; acetic, s.; chloracetic, v.s.; dichloracetic, v.s.; trichloracetic, v.s.; bromacetic, v.s.; dibromacetic, v.s.; propionic, s.; α-bromopropionic, v.s.; β-bromopropionic, s.; normal butyric, s.; isobutyric, v.s.; valerianic, s.; capronic, s.; œnantholic, s.s.; caprylic, s.s.; caprinic, s.s.; pelargonic, n.s.; myristinic, n.s.; palmitic, n.s.; margaric, n.s.; and stearic, n.s. **Dibasic acids**: oxalic, n.s.; malonic, n.s.; succinic, n.s.; pyrotartaric, n.s.; diacetylsuccinic, v.s.; and dibromosuccinic, s.s. **Esters**: ethyl formate, m.; amyl formate, m.; acotoacetic, m.; propyl acotate, m.; isobutyl acetato, m.; amyl acetate, v.s.; capryl acetate, s.s.; methyl propionate, m.; propyl propionate, v.s.; amyl propionate, s.; methyl butyrate, m.; ethyl butyrate, m.;

amyl butyrate, s.s.; isobutyl butyrate, s.; ethyl valeriate, v.s.; amyl valeriate, s.s.; isobutyl valeriate, s.; ethyl caprylate, s.s.; ethyl pelargonate, s.s.; ethyl oxalate, n.s., forming oxamide; ethyl malonate, m.; ethyl succinate, m.; ethyl lactate, m.; ethyl tartrate, m.; ethyl citrate, m.; ethyl carbonate, m.; tributyrine, m.; and amyl nitrite, s. **Cyanogen compounds:** methyl and ethyl cyanides, m.; cyanuric acid, s.; ethyl thiocyanate, m.; ethyl isothiocyanate, v.s.; and paracyanogen, n.s. **Amines:** methyl, m.; trimethyl, m.; diethyl, s.; dipropyl, s.; amyl, m.; diamyl, s.s.; tetramethylammonium chloride, s.s.; tetramethylammonium hydroxide, s.s.; tetramethylammonium iodide, s.s.; and hydroxylamine chloride, v.s. **Amido-acids:** glycine, amidopropionic acid, leucine, sarcosine (methyl glycerol), and tryosine, v.s. **Acetamide and ureides:** formamide and acetamide, v.s.; dichloroacetamide, cyanacetamide, thioacetamide, phenylacetamide and propionamide, v.s.; oxamide, s.s.; succinamide, s.s.; asparagin, creatine, and urea, s.; urea nitrate, thiourea, alkyl thiourea, urethane, allylthiourethane, and sulphocarbanilide, v.s.; uric acid, s. (n.s.); guanidine nitrate, v.s.; theobromine, alloxantine, parabanic acid, and dialuric acid, s.; uranil, v.s.; murexide, s.; and alloxan, v.s. **Hydroxy-acids:** glycolic acid, v.s.; lactic acids, v.s.; malonic, acid, s.s.; tartaric acid, s.s.; citric acid, s.s.; muconic acid, s.; and oxyisobutyric acid, v.s. **Sugars:** cane-sugar, v.s.; arabinose, s.; glucose, v.s.; fructose, v.s.; galactose, s.; phenylglucosazone, lactose, maltose, and raffinose, v.s. **Ethylene derivatives:** amylene, n.m.; allyl alcohol, m.; allyl isothiocyanate, m.; oleic acid, n.s.; maleinic acid, n.s.; fumaric acid, n.s.; citraconic acid, s.s.; itaconic acid, n.s.; mesaconic acid, s.s.; aconitic acid, s.; and crotonic acid, s.

Aromatic compounds.—**Hydrocarbons:** benzene, s.; toluene, s.s.; *o*-xylene, *m*-xylene, *p*-xylene, and ethylbenzene, s.s.; mesitylene, n.s.; cumene, pseudocumene, cymene, diphenylmethane, and triphenylmethane, n.s.; and diphenyl, s.s. **Halides:** chlorobenzene, bromobenzene, iodobenzene, hexachlorobenzene, dibromobenzene, and *p*-chlorotoluene, s.s. **Nitro-compounds:** nitrobenzene, v.s.; dinitrobenzene, s.; *o*-nitrotoluene, s.; *p*-nitrotoluene, s.s.; 1–2–4-trinitrotoluene, s.s.; trinitrotoluene, s.; *m*- and *p*-nitrochlorobenzene, s.s.; and *m*-nitro-*p*-chlorotoluene, s. **Amido-compounds:** aniline, *m*; *o*-toluidine, m.; *p*-toluidine, v.s.; *m*-nitro-*p*-toluidine, v.s.; asymmetric *m*-xylidine, s.s.; dimethyl- and diethyl-aniline, s.s.; methyldiphenylamine, s.s.; *m*- and *p*-nitraniline, v.s.; and picramide, v.s. **Phenols:** phenol, v.s.; *o*-, *m*-, and *p*-cresol, m.; pyrocatechol, resorcinol, hydroquinone, pyrogallol, orcin, and thymol, v.s.; guaiacol, anisol, and phenetol, m.; and menthol, s. **Substituted phenols:** *o*-, *p*-, 1–2–4-, and tri-nitrophenol, v.s.; *p*-nitroanisol, s.s.; eugenol, s.; anethol or phenethol, s.s.; and *o*- and *p*-amidophenol, v.s. **Alcohols, ethers, and aldehydes:** benzyl and cinnamic alcohols, m.; benzylethyl ether, s.s.; benzaldehyde, v.s.; anisaldehyde, m.; *m*-nitrobenzaldehyde, v.s.; cinnamic aldehyde, m.; vanillin, v.s.; and heliotropine, v.s. **Monobasic acids:** benzoic, benzoic anhydride, and *o*- and *m*-toluic, v.s.; *p*-toluic, s.; cinnamic, s.; *m*-bromobenzoic, v.s.; *o*- and *m*-nitrobenzoic, s.; *p*-benzoic, s.s.; *o*-, *m*-, and *p*-amidobenzoic, v.s.; *o*- and *m*-oxybenzoic, s.s.; *p*-oxybenzoic, s.s.; *o*-nitrocinnamic, v.s.; and nitrophenylpropiolic, gallic, anisic, and cumaric, s. **Diabasic acids:** *o*- and *p*-phthalic acid, s.s.; and phthalimide, v.s. **Esters:** methyl benzoate, m.; ethyl benzoate, v.s.; isobutyl benzoate, and amyl benzoate, n.s.; methyl salicylate, s.; phenyl and benzyl cyanides, m.; *p*-tolyl cyanide, v.s.; phenyl acetate, m.; phenyl salicylate, s.s.; phenyl isosulphocyanate, s.; and ethylphenyl urea, v.s. **Sulphoacids:** benzene sulphochloride, reacts; *o*-amidobenzene sulphonic acid, v.s.; *m*- and *p*-amidobenzenesulphonic acids, v.s.; benzosulphinic acid, and saccharine, s. **Acid amides and acid anilides:** formanilide, and acetanilide, v.s.; *p*-acetotoluidine, s.s.; benzamide, and *p*-chlorobenzamide, v.s.; benzanilide, s.s.; hippuric acid, v.s.; benzoylsulphamide, v.s.; *m*- and *p*-methoxybenzenesulphamide, and toluenesulphamide, v.s.; and carbazol, s. **Naphthalenes:** naphthalene, s.s.; α-naphthol, s.; β-naphthol, s.s.; α-naphthylamine, v.s.; β-naphthylamine, s.; nitro-β-naphthol, s.; and acetonaphthylamine, s.s. **Pyridine and quinoline:** pyridine, picoline, and collidine, m.; nicotine, s.; quinoline, m.; isoquinoline, s.s.; and dihydrocollidine dicarbonate, s.s. **Terpenes:** terebene, n.s.; carvene, and carvol, s.s.; pinene, sylvestrene, and turpentine, n.s.; borneo camphor, s.; and camphoric acid, n.s. **Miscellaneous:** acetophenone, and alizarin, s.; amygdaline, v.s.; anthracene and anthraquinone, n.s.; gun-cotton (s.s.); benzil, s.; benzoin, n.s.; brucine, s.; quinine hypophosphite, s., iodide, n.s., and sulphate, n.s.; quinone, and chloranil, s.; cholesterin, n.s.; cinchonin, n.s.; cinchonidine, s.s.; cocaine, n.s.; cocaine chloride, s.; codein, s.; codein nitrate, n.s.; cubebin, v.s.; digitalin, v.s.; fish-glue, syrupy; gum arabic, s.; guttapercha, reacts; hæmoglobin, s.s.; hæmatoxyline, s.; indigo (s.s.); camphor (v.s.); copal resin (s.s.); meconine, morphine, and narcotine, n.s.; phenanthrene, n.s.; phloridizine, and β-phthaldiadoxime, v.s.; piperidine, s.s.; piperine, n.s.; salicine, v.s.; santonine, n.s.; silk, n.s.; starch, swells; strychnine, acetate, bromide, and chloride, n.s.; tannin, s.s.; and theine, s.s.

F. de Carli obtained the following results for the solubilities of various organic compounds in liquid ammonia: *Benzene*, s.s., colourless; *toluene*, s.s., colourless; *ethyl benzene*, n.s., colourless; *nitrobenzene*, 24 per cent., yellow; *cumene*, s.s., yellow; *propylbenzene*, n.s.; *m-xylene*, s.s., colourless; *dinitrobenzene*, 19 per cent., red; *p-nitrochlorobenzene*, s.s., violet; *p-dibromobenzene*, n.s.; *o-nitrobenzene*, s.s., carmine; *cimene*, s.s., yellow ; *mesitylene*, s.s., colourless ; *dinitrotoluene*, s.s., blue ; *pseudocumene*, s.s., yellow ; *butylbenzene* (*tert.*), n.s. ; *hexachlorobenzene*, n.s. ; *m-dimethylcyclohexane*, n.s. ; *naphthalene*, n.s. ; *α-nitronaphthalene*, s.s., red ; *tetrahydronaphthalene*, n.s. ; *decahydronaphthalene*, n.s. ; *fluorene*, n.s. ; *anthracene*, n.s. ; *phenanthrene*, n.s. ; *dibenzil*, n.s. ; *stilbene*, s.s., colourless ; *diphenylmethene*, n.s. ; *triphenylmethane*, n.s. ; *acetanaphthene*, n.s. ; *benzyl alcohol*, m., colourless ; *menthol*, 16 per cent., colourless ; *benzoic aldehyde*, 82 per cent., yellow ; *salicylic aldehyde*, s.s., yellow ; *anisic aldehyde*, 70 per cent., yellow ; *cinnamic aldehyde*, s.s., yellow *cuminic aldehyde*, s.s., yellow ; *acetophenone*, s.s., colourless ; *benzylacetone*, s.s., yellow ; *phenic acid*, m., yellow ; *benzoic acid*, 46 per cent., colourless ; *salicylic acid*, m., colourless ; *o-nitrobenzoic acid*, 38 per cent., orange ; *sulphanilic acid*, 28 per cent., yellow ; *phthalic acid*, n.s. ; *picric acid*, 52 per cent., red ; *tetrachlorophthalic acid*, n.s. ; *cinnamic acid*, 6 per cent., yellow ; *benzyl acetate*, m., yellow ; *amyl salicylate*, s.s., colourless ; *ethyl cinnamate*, s.s., yellow ; *benzonitrile*, m., yellow ; *benzamide*, 35 per cent., yellow ; *p-toluidine*, 41 per cent., yellow ; *o-nitraniline*, 15 per cent., red ; *acetanilide*, 48 per cent., yellow ; *p-nitroanilide*, 10 per cent., yellow ; *benzilidenaniline*, n.s. ; *camphor bromide*, n.s. ; *pinene*, s.s., colourless ; *carvene*, n.s. ; *dimethylpyrone*, n.s. ; *phenylpyrrole*, n.s. ; *carbazole*, s.s., yellow ; *acridine*, s.s., yellow ; *thiodiphenylamine*, s.s., green ; *antipyrine*, n.s. ; *amylene*, n.s. ; *caprylene*, n.s. ; *hexadecilene*, n.s. ; *malic acid*, n.s. ; *maleic acid*, n.s. ; *fumaric acid*, n.s. ; *oleic acid*, n.s. ; *palmitic acid*, n.s. ; *stearic acid*, n.s. ; *aconitic acid*, n.s. ; *thiourea*, 37 per cent., colourless ; *guanidinium carbonate*, n.s.

H. Stamm also measured the solubilities of the salts of the alkalies in liquid ammonia —potassium hydroxide, nitrate, sulphate, chromate, oxalate, perchlorate, persulphate, chloride, bromide, iodide, carbonate, and chlorate : rubidium chloride, bromide, and sulphate ; cæsium chloride, iodide, carbonate, and sulphate ; lithium chloride and sulphate ; sodium phosphate, phosphite, hypophosphite, fluoride, chloride, iodide, bromate, perchlorate, periodate, hyponitrite, nitrite, nitrate, azide, dithionate, chromate, carbonate, oxalate, benzoate, phthalate, isophthalate ; ammonium, chloride, chlorate, bromide, iodide, perchlorate, sulphate, sulphite, chromate, molybdate, nitrate, dithionate, thiosulphate, persulphate, thiocyanate, phosphate, phosphite, hypophosphite, arsenate, arsenite, amidosulphonate, ferrocyanide, carbonate, benzoate, methionate, phenylacetate, picrate, salicylate, phenylpropionate, benzoldisulphonate, benzolsulphonate, phthalate, trimesinate, mellitate, aliphatic dicarboxylates, tartrate, fumarate, and maleinate ; and phenol.

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§ 18. The Chemical Properties of Ammonia

Ammonia has a pungent, exciting odour ; animals die when submerged in the gas. When inhaled, the vapour irritates the nose and air-passages, causing a pungent sensation and sneezing. The eyes and nose water, and the pulse and respiration are accelerated. Ammonia causes a rise of blood-pressure, and stimulates the heart. M. von Pettenkofer [1] said that air laden with ammonia causes pneumonia —0·3 per cent. (in air) is dangerous, and 0·5 per cent. to those accustomed to it. According to J. Muck, and E. Hallervorden, small doses of ammonia act as a nerve stimulant. Conc. aq. ammonia reddens the skin, and with prolonged contact, it may produce a blister. If ammonia be introduced with the food, the urea discharge is augmented. P. P. Dehérain showed that small quantities have a toxic action on some plants ; while A. Müntz showed that ammonia can be assimilated by the nitric ferments. P. Mazé has studied this subject. Ammonia plays an important part in the physiology of plants, for it is converted by the nitric ferment—*vide supra*— into nitrates which are necessary food-stuffs. P. N. Prianichnikoff reported that in the higher plants ammonia plays an important part as the starting-point for the

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synthesis of protein and as an end-product in the oxidation of nitrogenous substances. It does not, however, accumulate as such, but is converted into asparagine. Plants may be divided into three types according to the facility with which they accomplish this synthesis of asparagine: (i) Plants which readily absorb ammonia from soln. and convert it into asparagine—*e.g. Hordeum sativum* (barley), *Zea mays* (maize), and *Cucurbita pepo* (pumpkin). (ii) Plants in which the absorption of ammonia is very feeble and in which the presence of ammonia in the culture soln. retards the oxidation of nitrogenous substances. The absorption of ammonia can be increased by adding calcium carbonate to the culture soln.—*e.g. Pisum sativum* (pea) and *Vicia sativa* (vetch). (iii) Plants in which the presence of ammonia in the culture soln. prevents the conversion of ammonia into asparagine—*e.g.* the yellow lupin (*Lupinus luteus*). The addition of calcium carbonate has no effect in these cases.

A. Smits[2] drew attention to H. B. Baker's observations on the change in the properties which occurs when some gases are intensely dried. He assumes that two different kinds of molecules are concerned in every phase: $\alpha\text{-}NH_3 \rightleftharpoons \beta\text{-}NH_3$; one kind is active, the other inactive. With intense drying, the equilibrium is shifted to the inactive side so that intensely dried ammonia contains only inactive molecules. W. Kuhn found that ammonia gas in quartz vessels is decomposed completely by monochromatic light of wave-length 2025–2140 A. at a speed proportional to the energy absorbed. Aq. soln. of the gas undergo no decomposition. The number of quanta absorbed by a mol of ammonia undergoing decomposition, varies from 2 to 2·5, and is independent of the press. (900 to 5 mm.). For temp. of 10°–20°, the speed of decomposition is independent of temp., and, generally, this speed is not affected by the size of the quartz surfaces (whereas the thermal dissociation is accelerated by quartz surfaces). The speed of decomposition is also unaffected by the addition of metallic sodium, and is therefore independent of the action of minute traces of water. With monochromatic light of $\lambda=2063$, the number of quanta necessary to decompose a mol of ammonia is 3·4, or as many as 10 if the monochromatization is very perfect. From the heats of dissociation for $N_2=N+N(-140,000$ cals.), $H_2=H+H(-84,000$ cals.), and $NH_3=0{\cdot}5N_2+1{\cdot}5H_2(-11,000$ cals.), whence $NH_3=N+H_2+H-123,000$ cals., and $NH_3=N+H+H+H-207,000$ cals., it follows that a quantum $h\nu$ for the ray 2063 corresponds with 128,000 cals. per mol. The energy furnished by the absorption of a quantum suffices for the first, but not for the second change. On these lines may be explained the facts that several quanta are required to decompose a mol of ammonia, and that the speed of decomposition depends on the degree of the monochromatization of the ultra-violet radiation. E. Warburg, A. Coehn and G. Prigent, E. Regener, and M. Berthelot and H. Gaudechon studied the photochemical decomposition of ammonia—*vide supra*. R. G. Dickinson and A. C. G. Mitchell, and H. S. Taylor and J. R. Bates studied the decomposition of ammonia by optically excited mercury atoms. C. Matignon concluded that some ammonia in the higher regions of the atmosphere is decomposed into its elements by the action of the ultra-violet light. E. Wourtzel observed that α-rays from radium decompose ammonia gas.

E. C. C. Baly and H. M. Duncan studied the decomposition of ammonia by means of a hot platinum wire. Two types of ammonia may be prepared—an inactive and an active modification—which are decomposed to different extents by the same quantity of energy. The active form is obtained by the slow withdrawal of ammonia from a cylinder containing the compressed gas; by warming the conc. aq. soln. and drying the gas by quicklime; and by isothermal evaporation of the liquefied gas at its b.p. The inactive form is obtained by the rapid evaporation of the liquefied gas. The inactive gas slowly recovers its activity on remaining in contact with the liquefied gas. The same effect can be produced by gently warming the gas by means of a platinum wire heated at 200°. In order to observe these phenomena, the platinum wire must be activated in the same way as is customary in W. Ostwald's process for the catalytic oxidation of ammonia in air to nitric acid. Alternatively, the activation may be effected by rapidly heating and cooling the wire for several hours. Active and inactive ammonia, passed alternately into the same decomposition vessel, give with a fixed supply of energy high and low decomposition values. When the same sample of ammonia is twice exposed to the heated wire, the ratios of the amounts decomposed in the two cases differ very materially with the two forms. The addition of water vap. increases the reactivity of ammonia, the increase being proportional to the amount of water vap. present. The enhanced reactivity is removed on drying the gas with quicklime. To summarize, the active and inactive forms of ammonia differ in the relative amounts of energy required for their decomposition. The phase of lower energy content is identical with that which is obtained when ammonia is completely freed from moisture, and it does not combine with hydrogen chloride. R. E. Burk found that the decomposition of ammonia on the surface of a heated molybdenum wire is of zero order. The presence of hydrogen produces a slight accelerating effect, whilst that of nitrogen produces a marked retardation, the velocity after first decreasing with increasing conc. of nitrogen attaining a final limiting value. The film of nitrogen on the surface of the wire is very persistent and is not removed by pumping off in vacuo. Wires, however, return to normal activity after performing one or more experiments with ammonia. Activated mols. only of nitrogen condense to form the poisoning film, which may consist of atomic nitrogen. Since the rate of reaction is not zero at nitrogen press. which are so great that the surface is almost completely covered, the reaction must still proceed on parts of the surface which are not poisoned or, at a reduced rate, on a film of nitrogen. The two possible mechanisms cannot be distinguished since both yield the same type of formula for the velocity of the reaction. At temp. between 1097° K. and 1228° K., the logarithm of the half-life varies linearly with the reciprocal of the absolute temp., the slope of the line corresponding with a heat of activation of 53,200 cals. This is a true heat of activation.

The decomposition of ammonia by heat, and the electrical discharge has already been discussed in connection with the synthesis of that gas. E. Regener found that ammonia is decomposed by ultra-violet light. **Hydrogen** has no action on ammonia or on its aq. soln. E. Böhm and K. F. Bonhöffer found that active hydrogen had no action on ammonia. A. T. Larson and C. A. Black measured the solubility of hydrogen in liquid ammonia between —25·2° and 22·0°, and 50–150 atm. press. According to J. J. Berzelius, ammonia is feebly combustible in **air**, for it burns with a pale yellow flame when in immediate contact with the flame of a candle, but the combustion does not continue without the extraneous flame. The gas does not support combustion in the ordinary sense of that term. N. R. Dhar and R. P. Sanyal found that when air or oxygen is passed into soln. of ammonia exposed to tropical sunlight, nitrites are formed ; and a mixture of ammonia and oxygen forms nitrogen. K. A. Hofmann and co-workers found that the oxidation of ammonia to nitrate by air proceeds readily at 380°–400° in the presence of a basic contact agent such as soda-lime and can be accelerated in an unusual degree by increase of pressure. Copper carbonate, nickel powder, silver powder, and nickel carbonate accelerate the reaction in order of increasing efficiency. Soda-lime may be replaced by the oxides or carbonates of the alkaline earths, provided that the maximum temp. does not exceed the temp. of decomposition of the corresponding nitrate. Technical nitrolim is readily nitrified at temp. below 200° if mixed with soda-lime and copper oxide and exposed in thin layers to the air during several days. In all the cases of oxidation of nitrogen described above, the presence of nitrite can be readily detected at the commencement of the action, particularly when oxidation takes place rapidly. Towards the end of the change, when the nitrate formation has attained its maximum, the nitrite content diminishes. The tervalent nitrogen of ammonia or its derivatives passes therefore into the tervalent oxidized condition in the nitrite, which, under the conditions of the experiments, is invariably oxidized to nitrate with considerable rapidity. G. Kassner obtained nitric acid by oxidizing ammonia by oxygen in the presence of a heated catalyst containing lead, manganese, alkaline earths, and oxygen.

M. Berthelot and H. Gaudechon observed that under the influence of ultra-violet rays a mixture of ammonia and oxygen forms water and nitrogen. Ammonia burns in oxygen, forming nitrogen, water, a small proportion of ammonium nitrate, and a trace of nitrogen peroxide. H. B. Jones found that nitric acid is formed during the combustion of an alcoholic soln. of ammonia. A. W. Hofmann showed that if ammonia be mixed with oxygen, say, by bubbling a stream of oxygen through a small quantity of a conc. soln. of ammonia warmed in a flask, the gas issuing from the flask can be ignited; it burns with a greenish-yellow flame. In a few moments the soln. in the flask will be too dilute to show the flame. The experiment has been modified in various ways by W. Heintz, I. P. Ossipoff, M. Rosenfeld, A. Valentini, H. Schulze, D. L. Hammick, F. Brandstätter, S. Lupton, O. Wehrheim, W. R. Hodgkinson and F. K. Lowndes, and A. Klages. By sending a jet of ammonia into the air-holes of a Bunsen's burner, the flame will be found to expand, and acquire a yellow tinge. The effect is shown better by delivering a jet of ammonia into the centre of the tube of a Bunsen's burner. If a stream of oxygen be sent into a cylinder, and a stream of ammonia be sent into the same cylinder through a wide glass tube, the ammonia can be ignited, and it will burn with a yellowish flame. The analysis of the gases in A. Smithell's flame separator shows that the yellow part of the flame is an effect of undecomposed ammonia, and not an effect of the union of nitrogen and oxygen. He also found that with the mixture of hydrogen and nitrogen, obtained by passing ammonia through a hot tube, in the first cone of the flame, the whole of the oxygen combines with hydrogen to form steam, which, with the nitrogen and excess of hydrogen, passes to the top of the outer tube, where this hydrogen burns with the outside air in a second flame. J. M. Eder examined the spectrum of ammonia burning in oxygen gas.

According to A. B. de Fourcroy, a mixture of two vols. of ammonia and one to six vols. of oxygen explodes when sparked; and when a mixture of ammonia and an excess of oxygen is passed through a red-hot tube, nitric acid is formed. G. B. Taylor represented the heat of the reaction: $4NH_3+5O_2=4NO+6H_2O+214,200$ cals., and $4NH_3+3O_2=2N_2+6H_2O+300,600$ cals.; and the rise of temp., $\theta=(75150x-2{\cdot}600y)(7{\cdot}08+3{\cdot}41x-0{\cdot}25y+8{\cdot}34V/B-V)$, where V denotes the partial press. of water-vapour; B, the total press. of the mixture of air, ammonia, and water-vapour; x, the mol. fraction of ammonia in the mixture; and y, the mol. fraction of nitric oxide produced in the oxidation.

F. Kuhlmann observed that a little nitric oxide and nitrogen peroxide are formed when a mixture of air and ammonia is passed through a red-hot tube. W. Henry showed that the flame of a burning substance is enlarged when the air is mixed with ammonia; and he was not able to make a mixture of air and ammonia which would detonate with the electric spark. H. Schlumberger and H. Piotrowsky said that mixtures of 16·5 to 26·8 per cent. by vol. of ammonia are explosive, and A. Reis found that the limits for the propagation of flame in ammonia-oxygen mixtures are below 15 and above 80 per cent. by vol. of ammonia. A. G. White found that in a tube 5 cms. in diameter, the ranges throughout which ammonia-air and ammonia-oxygen mixtures propagate flame, in vol. percentages of ammonia, are:

		Upwards.	Horizontal.	Downwards.
NH_3–Air	18°	16·1–26·6	18·2–25·5	none
	140°	16·0–28·7	17·0–27·5	19·9–26·3
	250°	14·0–30·4	15·9–29·6	17·8–28·2
	450°	12·3–33·9	13·5–33·1	14·4–32·0
NH_3–O_2	18°	15·3–79·0	16·7–79·0	18·1–79·0
	250°	—	14·8–79·0	15·8–79·0
	450°	—	12·6–79·0	13·5–79·0

A. G. White also calculated the flame temp. which ranged from 1610° to 1840°. He also studied the propagation of flame in mixtures of hydrogen and ammonia.

W. P. Jorissen studied the explosive limits of mixtures of ammonia, hydrogen, and air or oxygen; and represented the results by the triangular diagram, Figs. 37 and 38. J. R. Partington and A. J. Prince exploded mixtures of dry electrolytic gas and ammonia at 85° and 380 mm. press. so that no steam condensed. The mixture becomes explosive when the ratio of electrolytic gas to ammonia is just over unity, when 79 per cent. of the ammonia is decomposed. When the ratio is just above 3, the decomposition is complete, the sole products being steam, hydrogen, and nitrogen. When ammonia is exploded with a deficiency of oxygen, the excess of ammonia is completely decomposed into nitrogen and hydrogen, and oxides of nitrogen are formed only if the ratio of ammonia to oxygen is less that 1·6; the maximum oxidation of nitrogen is 16 per cent. with the ratio 1·22. The commencement of oxidation of nitrogen is marked by colour changes in the flame, which changes from yellow to green, violet, and white as the oxidation of nitrogen increases. When ammonia is exploded with oxygen, the amount of nitrogen oxidized is greater than in the explosion of a corresponding mixture of nitrogen, hydrogen, and oxygen. I. W. Cederberg studied the conditions for the catalytic combustion of explosive mixtures of ammonia and oxygen.

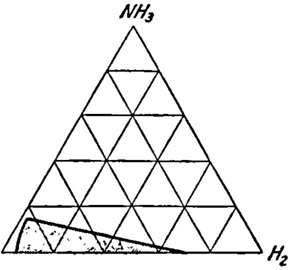

FIG. 37.—Explosive Limits in the System: H_2–NH_3–Air.

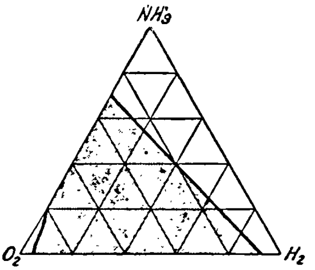

FIG. 38.—Explosive Limits in the System: H_2–NH_3–O_3.

J. W. Döbereiner found that platinum-sponge has no appreciable action on a mixture of equal vols. of ammonia and oxygen, but if the ammonia be mixed with electrolytic gas, the latter warms up the platinum and the ammonia is oxidized; W. Henry found that the mixture of equal vols. of ammonia and oxygen reacts in the presence of spongy platinum at 193°; F. Kuhlmann, in 1839, that the oxidation of ammonia occurs at about 300°, and that platinum-black is less efficient than spongy platinum; and C. F. Schönbein, that a heated platinum wire spiral in air charged with ammonia produces a white cloud of ammonium nitrate. D. Meneghini observed no action with a platinum spiral at 350°, but the reaction is vigorous between 400° and 450°. In K. Kraut's experiment, a stream of oxygen is sent through a conc. soln. of ammonia in a beaker in which is suspended a spiral of thin ($\frac{1}{4}$ mm.) platinum wire (recently ignited). If the current of oxygen be very slow, the platinum wire will glow red-hot, and the beaker will soon be filled with reddish-brown fumes of nitrogen peroxide. If the current of oxygen be faster, a small explosion will occur every now and again: the first explosion will be stronger than the second, the second stronger than the third, etc., and the soln. in the beaker will be found to contain both ammonium nitrite and nitrate. H. N. Warren used platinized ashes at a red-heat as a catalytic agent for the oxidation of ammonia, and the yields of nitrogen oxides with this catalyst were investigated by W. Reinders and A. Cats; O. Schmidt and R. Böcker—who, at a red-heat, obtained a 75 per cent. yield of oxides of nitrogen; and B. Neumann and H. Rose—who obtained a 96 per cent. yield at 500°. E. K. Rideal and H. S. Taylor found that during the action, the platinum swells up into microscopic efflorescences probably owing to the soln. of the gas and its subsequent expulsion. C. Schick employed platinized glazed-pottery, and this was said to have a longer life than platinum sponge. The subject was also discussed by M. Taliani, V. I. and N. A. Maliarewsky, L. Andrussoff, P. Pascal and E. Decarrière, H. A. Curtis, J. Baumann, W. S. Landis, A. A. Campbell, B. Neumann and H. Rose, and L. Cambi. E. Decarrière studied the catalytic action of palladium. P. Wenger and C. Urfer found that in the oxidation of ammonia, 97 per cent. is converted into nitric and nitrous acids by platinum-black as catalyst at 533°–562°; whilst with rhodium-black, a 69·7 per cent. oxidation is attained at 662°. L. Duparc and co-workers found rhodium more effective than platinum as catalyst.

W. Ostwald used corrugated platinum foil as catalyst, and he found that if the gas is not passed over the catalyst rapidly, ammonia is oxidized to nitrogen, $4NH_3+3O_2=2N_2+6H_2O$, but by taking suitable precautions, the ammonia can be oxidized to nitric oxide: $4NH_3+5O_2=4NO+6H_2O$. The heat of the nitric oxide reaction is 220 Cals., at ordinary temp., and is practically constant at 53 Cals. between 500° and 700°. The nitric oxide can be converted into nitric acid in the usual way—*vide infra*. At low temp., little or no nitric oxide is formed, but as the temp. rises, the rate of oxidation increases, reaching a maximum at about 750°, as indicated in Fig. 39. Beyond 750°, the ammonia decomposes into its constituents. F. C. Ziesberg described W. Ostwald's process. The reaction has been studied by F. G. Liljenroth, who showed that the heat of the exothermic reaction is sufficient to raise the temp. of the moving gas-mixture to 675° at the catalyst. If the initial temp. be 25°, the temp. of the catalyst will be raised to 700°. The smaller the percentage of ammonia oxidized, the smaller will be the heat developed during the reaction, and the lower the temp. of the catalyst. E. B. Andersen investigated the relation between the yield of oxide and the temp. and rate of flow of the gases.

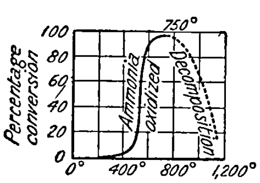

FIG. 39.—The Effect of Temperature on the Oxidation of Ammonia with Platinum as Catalytic Agent.

D. I. Mendeléeff supposed that an intermediate product, orthonitrous acid, $N(OH)_3$, is formed. Nitric oxide is the only compound which has been isolated in the oxidation of ammonia to nitrous or nitric acid. W. Reinders and A. Cats represented the reaction: $4NH_3+5O_2=4NO+6H_2O$, followed by $4NH_3+6NO=5N_2+6H_2O$; and $4NH_3+3O_2=2N_2+6H_2O$. The first reaction is accelerated by platinum or ferric oxide; the other reactions do not require a catalyst but are speeded up by glass or porcelain. F. Raschig does not accept the view that the combustion of ammonia in an excess of oxygen results in the formation of nitric oxide and water; and, if the ammonia is in excess, he writes: $4NH_3+3O_2=2N_2+6H_2O$. F. C. G. Müller found that under these conditions, the gaseous product contained 59 per cent. nitrogen and 41 per cent. hydrogen, and assumed that a portion of the ammonia dissociates into its constituent elements at the high temp. of the flame. If this were so, hydrogen ought also to be formed when oxygen is in excess, whereas under these conditions, 90 per cent. and more nitric acid is formed; nor is the ratio altered by cooling the flame. F. Raschig suggested that some hypothetical diimide is formed when the ammonia is in excess—$2NH_3+O_2=N_2H_2+2H_2O$—which would probably dissociate into hydrogen and nitrogen, and part of the ammonia may burn according to $4NH_3+3O_2=2N_2+6H_2O$, or else with the intermediate formation of hydrazine—$4NH_3+O_2=2N_2H_4+2H_2O$—which subsequently decomposes into nitrogen and hydrogen. F. Raschig proved that some hydrazine is actually formed when oxygen burns in ammonia. He therefore concluded that the main reaction in the combustion is $2NH_3+O_2=N_2H_2+2H_2O$, with the side reaction $4NH_3+O_2=2N_2H_4+2H_2O$. F. C. G. Müller found that the products of combustion of ammonia in oxygen contain hydrogen and nitrogen in the ratio 2 : 3; and this result is not altered by cooling the flame with cold water. Hence, it cannot be due to the dissociation of ammonia. F. Raschig's assumption that the equation $2NH_3+O_2=N_2H_2+2H_2O$ followed by the instantaneous dissociation of the diimide and partial combustion of the hydrogen does not account for the proportion of hydrogen produced. L. Andrussoff suggested that the group, NON, is an intermediate product, but J. R. Partington objected that if so, nitrous oxide might be expected as a by-product of the oxidation. This has not been found. E. Bodenstein assumed that the primary change involves the formation of nitrotyl: $NH_3+O_2=H_2O+HNO$, which is then converted, by oxygen, into nitric acid and then into nitric oxide, water and oxygen, or else, by ammonia, into nitrogen, water, and hydrogen. In the absence of oxygen or ammonia, the nitrotyl may form (*a*) nitrous oxide and water; (*b*) nitrogen, oxygen, and water; or (*c*) hydrogen and nitric oxide. J. Zawadzky and co-workers hold that the first step in the oxidation of ammonia is the dissociation of that compound into its constituent elements; atomic nitrogen then combines with oxygen to form nitric oxide, provided the temp. is not too high to allow the existence of this compound; otherwise the reaction $N+N=N_2$ will proceed at the expense of the reaction $N+O=NO$, and it is on the relative rates of these two reactions that the yield of the desired product depends. They do not agree with B. Neumann and H. Rose that the formation of nitrogen at a high temp. is due to the direct oxidation of ammonia to nitrogen and water, because in that case the reaction should be independent of the rate of flow of the gases and show a definite optimum temp., whereas equally good results can be obtained with higher temp. than the 500° used by B. Neumann and H. Rose, provided the rate of flow is suitably accelerated. Nitric oxide decomposes quite appreciably (12·2 per cent.) at 800°, and this decomposition is greatly assisted by contact with a platinum catalyst. The reason of the poor yields at temp. below 500° may be attributed to the reaction between ammonia and nitrogen trioxide and peroxide, whilst at higher temp. these oxides dissociate into oxygen and nitric oxide. According to Shun-Ichi Uchida, the catalytic oxidation of ammonia, $4NH_3+3O_2=2N_2+6H_2O$, occurs simultaneously with $4NH_3+5O_2=4NO+6H_2O$; he assumes, however, that the ammonia oxidizes to nitric oxide, which then, by a consecutive reaction decomposes by two concurrent reactions, $4NH_3+6NO=5N_2+6H_2O$, and $2NO=N_2+O_2$. The first of these reactions was shown by G. P. Baxter and C. H. Hickey to be very slow even in the presence of catalysts. When a stream of ammonia and air is passed at different speeds about a thin layer of a catalyst at a constant temp. the yield of nitric acid plotted against the time of contact with the catalyst yields a maximum. Shun-Ichi Uchida showed that the maximum can be explained by assuming that the resultant reaction involves the consecutive changes: $4NH_3+5O_2=4NO+6H_2O$ followed by $2NO=N_2+O_2$, and that the catalyst accelerates the two reactions at different rates. K. Jellinek, E. K. Rideal, and W. W. Scott discussed this second reaction as a source of loss in the oxidation of ammonia to nitric oxide. If the two reactions are unimolecular with the constant k_1 with respect to ammonia, and k_2 with respect to nitric oxide, the yield of nitric oxide C, at the time t, can be represented by $C=k_1(k_2-k_1)^{-1}(e^{-k_1t}-e^{-k_2t})$. With platinum gauze as catalyst, $k_1=5725$ per sec., and $k_2=31{\cdot}4$ per sec.; and with iron-bismuth as catalyst, $k_1=204{\cdot}5$ per sec., and $k_2=1{\cdot}17$ per sec. The maximum yield is then $C_m=(k_1/k_2)^{k_2/(k_2-k_1)}$ which is in agreement with observations. J. Baumann supposed the two reactions to be: $4NH_3+5O_2=4NO+6H_2O$, and $2NH_3+3O=N_2+3H_2O$; and S. Uchida, the rapid change $4NH_3+5O_2=4NO+6H_2O$, followed by the slow change $2NO=O_2+N_2$. The velocity constant for the first reaction is 180 times as large as that for the second.

Several industrial works have used the process of oxidation with the platinum plug as catalyst. A. Frank and N. Caro, G. Schäphaus, A. A. Campbell, and W. S. Landis have described the use of a single layer of electrically heated platinum gauze as catalyst for the oxidation of ammonia. K. Kaiser proposed the use of several superposed fine platinum or iridium gauzes in close contact, and preheating the gases at 300°–400° before passing to the catalyst so as to enable a rapid stream of gas to be passed through the system. J. R. Partington used two gauzes separated by narrow silica rods. The subject has been discussed by G. A. Perley,

E. Schlumberger, C. S. Imison and W. Russell, C. L. Parsons, and L. C. Jones. With platinum foil (W. Ostwald) and regenerative heating, J. R. Partington obtained a conversion efficiency of 90–95 per cent., and an output of 1·7 to 2·0 kgrms. of nitric acid per gram of platinum per 24 hrs.; with a single platinum gauze (A. Frank and N. Caro) and electrical heating, the respective numbers were 90–93 per cent. and 11 kgrms.; with four superposed platinum gauzes (K. Kaiser), 95 per cent. and 12 kgrms.; with two platinum gauzes slightly separated, with preheating of gases, 95 per cent. and 16 kgrms.; and with two platinum gauzes in contact, steam, and oxygen preheated to 500°–600°, 98–99 per cent. and 21 kgrms. The injurious effects of ammonia contaminated with phosphine, and acetylene have been discussed by C. L. Parsons, L. C. Jones, H. A. Curtis, and G. B. Taylor and J. H. Capps; 0·00002 per cent. of phosphine reduces the yield 30 per cent., and with 0·02 per cent. of phosphine the yield fell from 93·8 to 3·9 per cent. The presence of hydrogen sulphide counteracts the ill-effects of phosphine and of acetylene, but in general hydrogen sulphide has a baneful influence. E. Decarrière found that hydrogen to the extent of 0·44 per cent. has a slightly favourable influence, but with 1·0 to 1·5 per cent. it slightly reduces the activity of the catalyst; hydrogen phosphide reduces the activity 30 per cent., hydrogen sulphide partly neutralizes the baneful effect of hydrogen phosphide, and of acetylene. The subject was also studied by P. Pascal and E. Decarrière. Shun-Ichi Uchida found that the platinum catalyst evaporates slowly but distinctly at as low a temp. as 580°; this is not due to the scaling off of the activated surface. The loss of platinum was also observed by W. S. Landis.

A great many catalysts other than the preparations of platinum have been tried, but most have been found unsuitable—in some cases because of the small activity, in others because of rapid deteriorations; and in still others, an inconveniently high temp. may be required. In 1789, I. Milner found that ammonia is oxidized in contact with manganese dioxide, at a red-heat, producing nitrous acid and nitric oxide. Red-lead did not give this result, but ferrous sulphate which had been precalcined to whiteness gave better results. J. Black commenting on this result correctly explained the action in the following manner:

> The volatile alkali being a compound of hydrogen and azote, we need only suppose that part of it is totally decomposed and destroyed by the action of the oxygen contained in the manganese. Part of it, uniting with the hydrogen, forms water or watery vapour; and part, uniting with the azote, forms vapours of nitrous acid.

He also added that it was reported in the newspapers that " during the Napoleonic wars, the French chemists procured saltpetre for the army by blowing alkaline gas, and even putrid steams, through red-hot substances, like manganese dioxide, which readily yield oxygen." L. B. Guyton de Morveau, and L. N. Vauquelin oxidized ammonia to nitrates by passing it over hot manganese dioxide. C. S. Piggot studied the action of manganese dioxide alone and when mixed with copper or silver oxide, and also of silica and of various alloys of manganese, copper, silver, and iron. A mixture of manganese oxide with 40 per cent. of copper has a 90 per cent. efficiency at 800°. W. Manchot and J. Haas examined silver oxide intimately mixed with pumice as catalyst. H. G. Kreul used ferric oxide with 5 per cent. bismuth oxide as catalyst; and the General Chemical Co., an ignited mixture of aluminium and cobalt nitrates. The general subject was examined by M. Guichard. G. Kassner oxidized ammonia to nitric acid by means of a catalyst he called *nitroxan*, which is a compound or equimolar mixture of metaplumbate and manganate of barium, and is made by heating in air a mixture of barium orthoplumbate and manganese dioxide in the correct proportions. The reaction is probably as follows: $2BaPbO_3,BaMnO_4+NH_3=HNO_3+2BaPbO_2+2BaMnO_3+H_2O$; $BaPbO_2+BaMnO_3+O_2=BaPbO_3,BaMnO_4$. The nitric acid is retained as barium nitrate, which is adsorbed as such by the substance of the catalyst. When the reaction is carried out at 600°, *i.e.* above the decomposition temp. of barium nitrate, the products contain an excess of nitrogen peroxide, which, in the presence of oxygen and the water which is formed, is rapidly condensed to liquid nitric acid. Poor yields are obtained when the barium nitrate is formed at a low temp. (260°–450°), and is then decomposed by raising the temp.; the ammonia is never completely oxidized in the first part of the reaction and nitric oxide is formed which reacts with free ammonia with the formation of nitrogen, especially if any uncombined manganese dioxide is present in the catalyst. By lixiviating the barium nitrate from the catalyst and replacing the barium thus removed by finely-powdered barium hydroxide, better yields are obtained, the catalyst improving with use. In this way a 100 per cent. conversion of ammonia into nitric acid may be obtained. J. von Liebig found that the reaction is catalyzed by ferric oxide; and A. F. de Fourcroy, by mercuric oxide. The last-named called the reaction *une décomposition réciproque.* F. Kuhlmann found that copper hydroxide, copper, nickel, and iron are less active than platinum. R. Marston proposed copper as catalyst; E. Aubertin, chromic oxide and chromates; C. M. Tessié du Motay, manganates, permanganates, dichromates, and alkali plumbites; H. Schwarz, sodium manganate; L. C. Jones and co-workers, plumbites of aluminium, zinc, or cadmium; C. L. Parsons, lead oxide on bone-ash at 100°; A. Frank and N. Caro, ceria and thoria; B. Neumann and H. Rose, ferric oxide at 670°. K. Inaba studied a mixture of iron and bismuth oxides as catalyst, and the yield was increased in the presence of thoria. The Badische Anilin- und Soda-fabrik recommended oxides of the iron group; F. Bayer and Co., iron oxide, and promotors—cerium or bismuth oxides—at about 800°; that company also proposed iron oxide with bismuth oxide; iron oxide with tellurium; and platinum with lead. B. Neumann and H. Rose examined the effect of iron-bismuth oxide at 600°; D. Meneghini tried roasted pyrites, chromic oxide, or oxides of the rare earths—ferric, manganic, and ceric oxides were less active; W. Reinders and A. Cats compared platinized asbestos, or glass, copper wire, thorium oxide and pumice, ferric oxide on glass or asbestos, and oxidized iron-gauze. They found 80–90 per cent. oxidation with platinum, or ferric oxide. Ferric oxide worked best at 650°–700°; and platinized asbestos or glass, at 600°. N. Smith found that stannic and manganic oxides oxidize ammonia to nitrate and nitrite at ordinary temp.; ferric oxide and lead dioxide have but a slight action. Various oxides—copper, silver, vanadium, chromium, molybdenum, lead, manganese, cobalt, and nickel—have been tried. E. B. Maxted found that the percentage conversion with iron catalyst activated with the promotors copper, thorium, tungsten, cerium, or bismuth, at 700°, when the time of contact of the gas-mixture with the catalyst is 0·015 sec., is as follows, when iron alone gave 83·5 per cent. conversion:

	Fe(Mn)	Fe(Cu)	Fe(Th)	Fe(W)	Fe(Ce)	Fe(Bi)
Per cent. conversion	75·0	86·0	87·3	89·3	90·0	92·0

The relative efficiency with different rates of flow of the gas-mixture is illustrated by Fig. 40, where the speed of flow is expressed in litres per hour per c.c. of free space in the reaction chamber—calculated at room temp. Each c.c. of free space corresponds with 20 sq. cms. of catalyst surface. E. I. Orloff observed the oxidation of ammonia when mixed with air and passed over a heated copper gauze: $4NH_3+3O_2=2N_2+6H_2O$, with traces of nitrous and nitric acids—aniline, toluidine, and pyridine were oxidized in a similar way. W. W. Scott and W. D. Leech found that the conversion efficiency of cobalt oxide at 600°–800° is 79·3 per cent. This is augmented when about 3 per cent. of bismuth, or 10 to 12 per cent. of alumina, is used as promotor. The efficiency is then increased up to 90 per cent. Metals with m.p. below that of cobalt act as stimulants of the reaction, while metals with a higher m.p. retard the reaction. Observations on the subject were made by W. Kochmann, W. Moldenhauer and O. Wehrheim, H. Petersen, N. Busvold,

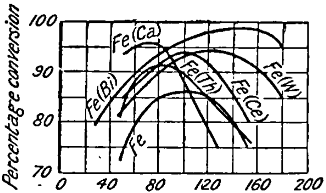

FIG. 40.—Efficiency of Catalysts in the Oxidation of Ammonia.

P. Wenger and C. Urfer. N. Smith found that in the oxidation of tin or copper in air, ammonia is simultaneously oxidized—induced reactions; zinc has no action, but in glass dishes positive results were sometimes obtained—while only a slight action was observed in the oxidation of ferrous and manganous hydroxides.

In practice, where nitric acid is made by the oxidation of ammonia, the catalyst employed may be a platinum plug (W. Ostwald); an electrically heated wire gauze (K. Kaiser); or iron activated by another metal. The most satisfactory catalyst is platinum gauze of fine mesh, or platinum foil whose smooth surface is roughened by a deposit of platinum-black. Platinum sponge, or platinum-black alone is much too active. A thin layer of catalyst gives the best results, because with a thick layer, or a low velocity, some nitric oxide is decomposed. The platinum gauze processes can be illustrated by A. Frank and N. Caro's reaction chamber. At the bottom, air enters on one side, ammonia on the other. Valves are provided so that the correct proportions can be regulated. The gases are mixed by a revolving aluminium fan and then pass through the heated platinum gauze. The gauze is electrically heated to 700°, but once the reaction commences, in some arrangements, the heat developed by the reaction suffices to keep the gauze red-hot. The lower half of the casing of the reaction chamber is cooled by water so as to prevent, as far as possible, the thermal decomposition of the ammonia by the heat radiated from the gauze. The combustion chamber is lined with aluminium so as to prevent any iron oxide from falling on the platinum gauze. The industrial oxidation of ammonia to nitric acid has been discussed by E. Donath, J. R. Partington, O. Dieffenbach, A. M. Fairlie, E. J. Pranke, P. J. Fox, A. Frank and N. Caro, H. J. M. Creighton, W. G. Adam, C. S. Imison and W. Russell, P. Pascal and E. Decarrière, C. L. Parsons, A. T. Schlösing, V. I. Maliarewsky, and in many anonymous articles.

According to C. F. Schönbein, D. K. Tuttle, E. M. Peligot, and M. Berthelot and L. P. de St. Gilles, when copper is immersed in an aq. soln. of ammonia, it is oxidized, when exposed to air, and ammonia is simultaneously oxidized to nitrite; S. Kappel said that some nitrate is also formed. E. Müller found that with small proportions of dissolved copper in the catalytic oxidation of aq. ammonia to nitrite by oxygen in the presence of sodium hydroxide, the velocity of the reaction is proportional to the conc. of copper, to the press. of the oxygen, and to the conc. of the hydroxyl ions. The speed of nitrite formation increases with increasing conc. of ammonia, and with rise of temp. The presence of ammonium salts retards the change by removing hydroxyl ions. With solid copper, the activity is due to the presence of copper in soln., forming cuprous ions which are very active; and solid cuprous oxide is an active catalyst. The changes of potential of a copper anode in $2N$-NaOH, in the presence and absence of ammonia, are consistent with the hypothesis that tervalent copper ions play an intermediate rôle in the mechanism of the catalysis. Thus, bivalent copper ions may form tervalent ions by means of charges from hydrogen ions oxidized to water; the tervalent ions then react with hydroxyl ions in the presence of ammonia to give nitrite ions and reform bivalent copper ions. Similarly with cuprous ions. The hypothesis, thus expressed in the language of ions, means that the catalytic activity of copper is attributed to the capacity of copper to form higher oxidation products in soln.

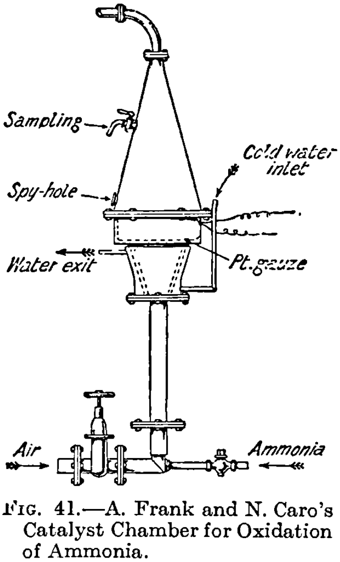

FIG. 41.—A. Frank and N. Caro's Catalyst Chamber for Oxidation of Ammonia.

W. Traube and A. Biltz found that in the electrolysis of an aq. soln. of sodium hydroxide containing ammonia, using platinum or iron electrodes, and a current of 5 to 10 ampères, virtually no nitrite is formed, but if some copper hydroxide be present, almost all the oxygen evolved at the anode is consumed in converting the ammonia into ammonium nitrite. As the electrolysis proceeds, the amount of nitrite formed gradually increases, and then, after a certain time, decreases owing to the oxidation to nitrate; if the electrolysis be continued for a considerable time, the liquid at the anode is found to contain only nitrate and no nitrite. A soluble alkaline earth may be substituted for the fixed alkali. When no free alkali is present, the formation of nitrite ceases, but if care is taken to keep the anode compartment permanently alkaline, the production of nitrite continues until a very concentrated soln. is obtained. In addition to the nitrite formation, a small amount of nitrate is also produced at the expense of the nitrite. The amount of this is small at the beginning, but tends to increase, even when an excess of alkali is present, as the ratio of the conc. of the nitrite to the conc. of ammonia increases. The conversion of nitrite into nitrate in the strongly alkaline liquid is accelerated by the presence of small amounts of cupric hydroxide. If the amount of alkali hydroxide in the anode compartment becomes less and less and finally completely disappears, so that at the end only an ammoniacal soln. is present, it is found that a rapid oxidation of nitrite to nitrate occurs, but even this is accelerated by the presence of the cupric hydroxide so long as free alkali is still present. In presence of much ammonia, the amount of nitrite can be increased to about 11 per cent. before oxidation to nitrate begins, whilst from an 11 per cent. nitrite soln. to which ammonia, sodium hydroxide, and copper hydroxide had been added a soln. containing as much as 17 per cent. nitrite was obtained on hydrolysis. E. Müller and F. Spitzer said that the electrolytic oxidation of ammonia to nitrite occurs in the presence of sodium hydroxide even in the absence of copper compounds. A. Brochet and G. Boiteau found that when an aq. soln. of ammonia is electrolyzed, using electrodes of graphite, a mixture of ammonium carbonate and nitrate is produced. The quantity of nitrate formed increases if ammonium carbonate or nitrate is first added to the soln. A similar reaction takes place if platinum or iron electrodes are used to electrolyze soln. of ammonium carbonate or nitrate in ammonia. The yield of nitrate was always low, it increases with current density, and the rate of formation decreases when the conc. of nitrate in soln. is high. G. Oesterheld electrolysed a sat. ammoniacal soln. of ammonium carbonate, and cooled the washed and dried gases. The mixture has a colour which may be exactly imitated by dipping a test-tube containing liquid air in liquid nitrogen trioxide, and, after a frozen layer has been formed, in liquid nitrogen tetroxide. The two layers of blue and yellow give a green which is exactly like that of the supposed hexoxide. The electro-oxidation of ammonia has been investigated by F. Balla, F. Grieshaber, etc.

According to T. P. Blunt, a mixture of ammonia and air may be kept in darkness without change, but in light there is a reaction attributed to the formation of ozone. L. I. de N. Ilosva found that **ozone** does not act on dry ammonia; but F. M. Baumert found that with ozonized oxygen and ordinary ammonia gas, clouds of ammonium nitrate are formed. L. Carius passed ozonized oxygen into an aq. soln. of ammonia, and found that some ammonium nitrite and nitrate are formed as well as a little hydrogen dioxide. The reaction was studied by F. Goppelsröder. W. Strecker and H. Thienemann observed that ozone is completely reduced when passed into liquid ammonia cooled by a mixture of carbon dioxide and ether. The products of the reaction contain about 98 per cent. of ammonium nitrate and 2 per cent. of nitrite: $2NH_3+4O_3=NH_4NO_3+4O_2+H_2O$; and $2NH_3+3O_3=NH_4NO_2+3O_2+H_2O$. When ozone is first passed into the liquid an orange colour is produced which may be due to the formation of an unstable ozonide. Carefully dried ozone at first acts very slowly on liquid ammonia. W. Weith and A. Weber reported that **hydrogen dioxide** and aq. ammonia react, forming nitrous acid or ammonium nitrite; on the contrary, F. Hoppe-Seyler could find no nitrite as a result of keeping a conc. soln. of hydrogen dioxide in contact with ammonia

—with or without the addition of sodium hydroxide—but if the soln. be evaporated in a retort at its b.p., the nitrite is formed. According to W. R. Hodgkinson and A. H. Coote, if an ammoniacal soln. of hydrogen dioxide be allowed to act for 5 mins. on pieces of metal approximately the same size, the losses in weight are: cadmium, 7 per cent.; copper, 1·4 to 3·6 per cent.; zinc, 3·9 per cent.; copper-nickel alloy, 0·1 per cent.; and in the presence of an ammoniacal soln. of hydrogen dioxide and ammonium nitrate, the losses were, cadmium, 18 per cent.; copper-nickel alloy, 1·0 per cent. A. W. Browne and O. R. Overman observed no indication of the formation of appreciable quantities of nitrous or nitric acid when ammonium sulphate in sulphuric acid soln. is treated with oxidizing agents such as hydrogen dioxide; potassium chlorate, persulphate, permanganate, or iodate; hydrated ferric oxide; or mercuric oxide or chloride. Ammonium sulphate soln. strongly acidified with sulphuric acid is but slightly affected at the b.p. by such oxidizing agents as hydrogen dioxide, or potassium chlorate or permanganate. F. Kuhlmann oxidized the whole of the nitrogen in ammonium sulphate to nitrite by treatment with potassium chlorate; and to nitrate by manganese dioxide, the higher lead oxides, or potassium permanganate and sulphuric acid. C. F. Schönbein, and F. Wöhler found that an aq. soln. of ammonia is oxidized by manganese dioxide when the mixture is shaken along with platinum sponge. S. Cloez and E. Guignet said that in the cold, ammonia is oxidized to nitrite by potassium permanganate, and to nitrate when heated with an excess of the permanganate; and L. P. de St. Gilles said that the oxidation proceeds rapidly if formic acid be also present. P. A. Bolley said that the ammonia is not oxidized by potassium permanganate if the soln. be very dil. O. T. Christensen observed the formation of nitrate during the decomposition of ammonium permanganate by heat.

According to H. Moissan,[3] **fluorine** reacts with ammonia with the production of a yellow flame, while with a soln. of ammonia each bubble of fluorine gives a flame accompanied by a detonation. The gas burns at ordinary temp. in **chlorine**, forming ammonium chloride and nitrogen: $8NH_3+3Cl_2=6NH_4Cl+N_2$. A. Valentini devised an apparatus for demonstrating this. F. Donny and J. Mareska found that strongly cooled liquid chlorine reacts vigorously with ammonia. According to P. L. Simon, when chlorine is passed in successive bubbles into conc. aq. ammonia, each bubble produces a slight explosion, and a flash of light, visible in the dark. If the ammonia be in excess, nitrogen is evolved, and ammonium chloride is formed; but if an excess of chlorine acts on ammonia, or on an ammonium salt, nitrogen chloride is produced—*vide infra*, nitrogen chloride. A. J. Balard, and E. J. Maumené said that by rapidly mixing chlorine water and aq. ammonia, hydroxylamine chloride is formed. A. J. Balard found that **bromine** reacts with ammonia, forming nitrogen and ammonium bromide. According to A. Bineau, ammonia gas reacts with **iodine** in the cold, forming a viscid liquid which, when treated with water, decomposes into ammonium iodide, nitrogen iodide, and hydrogen. In the presence of alcohol, iodine decomposes ammonia, forming ammonium iodide, diiodoamide, and nitrogen iodide. W. H. Seamon obtained what he regarded as *amminodiiodide*, NH_3I_2, by the action of dry ammonia on dry iodine, and allowing the product to stand for some time over conc. sulphuric acid. F. Raschig said that the product of the reaction between dry iodine and ammonia depends on the temp. C. Hugot, and O. Ruff obtained a number of different substances by the action of iodine on liquid ammonia—*vide infra*, nitrogen iodides. C. F. Schönbein found that the product of the action of aq. ammonia and iodine water has bleaching qualities and probably contains ammonium hypoiodite; some ammonium iodide and iodate are also formed. For the action of the **hydrogen halides**, and of the **halide acids**, *vide* the corresponding ammonium salts. L. Troost, working with dried ammonia and hydrogen chloride, obtained *ammonium hexamminochloride*, $NH_4Cl.6NH_3$, melting at −18°; and *ammonium triamminochloride*, $NH_4Cl.3NH_3$, melting at 7°. The dissociation press. of the triammine is 140 mm. at −36°; 485 mm. at −13°; 730 mm. at −60°; 1035 mm. at 0°; and 1800 mm. at 8°. The hexammine has a dissociation press. of 580 mm. at —36° ; 750 mm. at —31·5° ; and 1130 mm. at —21°. A. J. Balard found that gaseous ammonia detonates in contact with **hypochlorous acid,** and chlorine is liberated, while a conc. aq. soln. is decomposed by ammonia gas with the liberation of free nitrogen and chlorine, and the evolution of heat and light ; in the cold, hypochlorous acid reacts with aq. ammonia, forming nitrogen chloride. Soln. of **sodium hypochlorite** decompose ammonia and ammonium salts evolving all the nitrogen as a gas. J. Thiele said that hydrazine and hydroxylamine are formed as intermediate products. T. Oryng found the reaction is of the second order ; and with the proportions $3NaOCl+2NH_3=3NaCl+N_2+3H_2O$, at 15°–25°, the oxidation of the ammonia to nitrogen is never complete. The effect of inert solvents is not alone determined by the viscosity. The reaction is accelerated by copper, mercury, lead, iron (ic), cobalt, nickel, titanium, platinum, manganese, and chromium salts. The reaction was also studied by A. Bineau, C. F. Schönbein, J. Kolb, H. J. H. Fenton, A. J. Balard, G. Lunge and R. Schoch, C. F. Cross and E. J. Bevan, J. Effront, and F. Raschig. Other products reported are nitrogen chloride (A. J. Balard, F. Raschig, and G. Lunge and R. Schoch), chloramide (F. Raschig), and chlorates (C. F. Schönbein). Soln. of **sodium hypobromite** or barium hypobromite, or a soln. of bromine water in alkali-lye decompose ammonia and ammonium salts as in the analogous case with hypochlorites. D. R. Nanji and W. S. Shaw observed that traces of nitrites and nitrates are formed during the reaction. F. von Stadion found that ammonia with **chlorine dioxide** furnishes at ordinary temp. nitrogen and ammonium chloride and chlorate. A. Ditte observed no action between ammonia and **iodine pentoxide** at ordinary temp., but when warmed, a vigorous reaction occurs with the formation of iodine, nitrogen, and water. G. Denigès found that when a drop of a 10 per cent. aq. soln. of iodic acid is exposed to an atm. containing ammonia, it immediately becomes covered with a crystalline film of the normal iodate, NH_4IO_3. None of the volatile amines examined give this reaction under these conditions. G. Denigès and J. Barlot added that if a drop of a 50 per cent. soln. of iodic acid is exposed to an atm. containing a trace of ammonia gas, it becomes covered with a thin white film, and if this is then well mixed with the iodic acid, rhombic crystals of ammonium tri-iodate can be observed under the microscope. If a drop of 50 per cent. iodic acid and a drop of conc. aq. ammonia are placed a few mm. apart on a microscope slide, the successive formation of the neutral iodate, the di-iodate, and the tri-iodate may be observed. K. A. Hofmann and W. Linnmann found that gaseous ammonia, mixed with air, reacts so vigorously with solid **potassium chlorate** that the reaction may become dangerous if the conc. of the ammonia is high. It is therefore advisable to dilute the chlorate by admixture with clay. The reaction begins at about 250°, and the heating is discontinued until the violence of the reaction has subsided. The course of the reaction is symbolized: $KClO_3+2NH_3 \rightarrow KCl+N_2+3H_2O$, and $KClO_3+N \rightarrow KNO_3+Cl$. The ammonia reacts directly with the chlorate and not with previously liberated oxygen, the change occurs at the surface of the chlorate and not in the gaseous layer, and the nitric acid is not formed intermediately. The incidence of the reaction is ascribed to the relatively unsaturated nature of the potassium chlorate and ammonia molecules and the consequent possibility of the production of intermediate additive products. In confirmation of this view, it is shown that the sat. potassium perchlorate mol. does not react with ammonia at moderate temp., and that, at higher temp., the production of nitrate is due entirely to the intermediate formation of potassium chlorate.

According to A. F. de Fourcroy,[4] if the vapour of **sulphur** and ammonia be led through a red-hot tube, hydrogen, nitrogen, and a crystalline mixture of ammonium mono- and poly-sulphides are formed. F. Jones said that dry sulphur absorbs ammonia, and when the product is heated, ammonium sulphide is formed. A. Smith and W. B. Holmes found that if ammonia gas be passed over molten sulphur no insoluble sulphur is formed during the cooling. C. A. Seely found that liquid ammonia dissolves sulphur, forming, according to H. Moissan, and C. Hugot, a soln. of *sulphoammonium.* E. C. Franklin and C. A. Kraus noted the dissolution of sulphur in liquid ammonia occurs only in the presence of air—*vide infra.* O. Ruff and E. Geisel found the reaction between sulphur and liquid ammonia is reversible: $10S+4NH_3 \rightleftharpoons 6H_2S+N_4S_4$. C. Brunner showed that aq. ammonia dissolves no sulphur at a temp. below 75°, or, according to F. A. Flückiger, below 60°–65°; but at 90° or in a boiling soln., the liquid acquires a pale lemon-yellow colour, while ammonium thiosulphate and sulphide are formed. J. B. Senderens said that a reaction occurs even at 12°; and F. A. Flückiger added that under press. in a sealed tube at 90°–100°, ammonia-water of sp. gr. 0·885 forms a deep yellowish-brown soln. of ammonium polysulphide, which, when the tube is opened, deposits crystals of sulphur. L. Troost obtained three *ammonium amminosulphides* by the action of ammonia on **hydrogen sulphide.** M. J. Fordos and A. Gélis showed that cold ammonia gas in contact with **sulphur dichloride,** SCl_2, produces brownish-red, or, with more ammonia, pale lemon-yellow flecks containing respectively the diammine, $SCl_2.2NH_3$, and the tetrammine, $SCl_2.4NH_3$; sulphur dichloride dropped slowly into an aq. soln. of ammonia was found by M. J. Fordos and E. Gélis to produce ammonium thiosulphate, sulphate, chloride, and sulphur amminonitride, and dichloride. E. Soubeiran, and K. Martens said that dry ammonia and **sulphur chloride,** S_2Cl_2, form a tetrammine, $S_2Cl_2.4NH_3$. A. K. Macbeth and H. Graham represented the reaction: $6S_2Cl_2+16NH_3=N_4S_4+12NH_4Cl+4S_2$, and added that other nitrogen sulphides—*e.g.* N_2S_5 and S_6NH_2—may be formed—*vide* the sulphur chlorides. The action of ammonia on **thionyl chloride** gives a white cloud of ammonium chloride, a yellow mass of nitrogen sulphide, and what A. Michaelis thought might be nitrogen chlorosulphide; H. Schiff said that thionyl amide is not formed. The reaction was discovered by H. Piotrowsky. H. V. Regnault said that **sulphuryl chloride** mixed with ethylene chloride reacts with dry ammonia, forming a mixture of sulphuryl amide, $(NH_2)SO_2$, and ammonium chloride. The reaction was further studied by A. Mente, F. Michel, A. Hantzsch and co-workers, and M. Traube, and it was shown that sulphimide, sulphomelide, sulphamide, nitrogen trisulphide, etc., were formed. H. Rose observed that when ammonia is passed slowly into cold **pyrosulphuryl chloride,** a white mass of the tetrammine, mixed with ammonium chlorosulphide, and sulphate is formed. According to J. W. Döbereiner, **sulphur dioxide** reacts with ammonia, forming a brownish-yellow vapour which condenses to a brown solid mass of anhydrous ammonium sulphite, which, with a small proportion of water, furnishes ordinary ammonium sulphite. H. Rose concluded that with the dry gases, an orange-red viscid or crystalline mass is produced which is very deliquescent, and dissolves easily in water, without evolving ammonia. The soln. is neutral, and when freshly prepared contains ammonium sulphite, sulphate, trithionate, etc. H. Rose supposed the orange-red substance to be a compound of ammonia with an isomeride of sulphur dioxide; G. Forchhammer, a mixture of ammonium sulphate, and sulphur diamide, $S(NH_2)_2$; H. Watts, a mixture of amidosulphinic acid, $NH_2.SO.OH$, and its ammonium salt; S. M. Jörgensen, ammonium pyroamidosulphinate, $NH_2.S_2O_4.NH_4$. E. Divers and M. Ogawa found that if the mixed gases are thoroughly dried, and at a low temp., no reaction occurs; but at a higher temp., with the sulphur dioxide in excess, a substance, ammonium amidosulphinate, $NH_2.SO.ONH_4$, or SO_2NH_3, is formed, and if the ammonia is in excess, amidosulphinic acid, $NH_2SO.OH$, or $SO_2(NH_3)_2$, is produced. The reaction was studied by H. Piotrowsky, and H. Schumann—*vide* amidosulphinites. When an ethereal soln. of ammonia is treated with sulphur dioxide, ammonium amidosulphinate is formed. For the action of **sulphur trioxide,** *vide infra.*

According to A. Loir and C. Drion, when liquid ammonia at −65° is poured on to conc. **sulphuric acid,** the liquids do not mix, and a reaction gradually sets in. According to V. A. Jaquelain anhydrous ammonia reacts with sulphuric acid, forming sulphamide, and, according to A. Woronin, ammonium amidosulphate, For sulphurous and sulphuric acids, *vide* the corresponding ammonium salts. R. Kempf represented the reaction with the **persulphate** resulting in the formation of nitrogen and a trace of nitric acid: $4Na_2S_2O_8+NH_3+9NaOH=NaNO_3+8Na_2SO_4+6H_2O$; and $3(NH_4)_2S_2O_8+8NH_3=6(NH_4)_2SO_4+N_2$. H. Marshall made some observations on this reaction. G. Scagliarini and G. Torelli said that in the oxidation of ammonia by either potassium or ammonium persulphate, the oxygen of the latter first oxidizes the ammonia to nitrous acid, which is converted by the excess of ammonia into ammonium nitrite, this being decomposed with liberation of nitrogen by the heat developed. Copper appears to act as an oxygen-carrier. D. M. Yost said that the rate of oxidation of aq. ammonia by the persulphate ion is directly proportional to the conc. of the oxidizing agent, and to the conc. of the catalyst—the $Ag(NH_3)_2$-ion. The rate of oxidation increases less rapidly than the rate of increase of the conc. of the ammonia. F. A. Flückiger said that **selenium** does not act on ammonia gas, or on aq. ammonia. E. C. Franklin and C. A. Kraus noted the dissolution of selenium in liquid ammonia occurs only in the presence of air. R. Epenschied showed that **selenium tetrachloride** reacts at ordinary temp. with dried ammonia mixed with air, forming selenium, ammonium chloride, nitrogen, and hydrogen; if the mixture be well-cooled, a brown mass of nitrogen selenide and ammonium chloride is formed. A. Michaelis obtained selenium, nitrogen, ammonium chloride, and selenium dioxide by the action of **selenyl chloride,** $SeOCl_2$; V. Lenher and E. Wolensensky found that with a benzene or toluene soln. of selenyl chloride, $SeOCl_2$, ammonia forms nitrogen selenide or a mixture of this and selenium. A. Michaelis represented the reaction with **selenium dioxide** by: $4NH_3+3SeO_2=6H_2O+3Se+2N_2$. R. Metzner gave for the reaction between **tellurium tetrachloride** and dry ammonia at 200°–250°: $3TeCl_4+16NH_3=3Te+12NH_4Cl+2N_2$; at 0°, tellurium triamminotetrachloride, $TeCl_4.3NH_3$, is formed.

A. T. Larson and C. A. Black[5] measured the solubility of **nitrogen** (*q.v.*) in liquid ammonia. E. J. B. Willey and E. K. Rideal found that ammonia is decomposed by activated nitrogen. W. Henry found that a mixture of **nitrous oxide,** with not less than one-seventh or more than three-fourths ammonia, explodes when sparked, forming water, nitrogen, and oxygen, and with an excess of nitrous oxide, nitrogen dioxide may be formed. G. Bischof said that some of the ammonia is decomposed into hydrogen and nitrogen. W. Wislicenus noted the action of sodamide on nitrous oxide, forming hydrazoates. W. Henry found that **nitric oxide** behaves towards ammonia in an analogous way to nitrous oxide when sparked. J. L. Gay Lussac found that a mixture of equal vols. of ammonia and nitric oxide gases condenses in the course of a month to about half its original vol., without undergoing complete decomposition—nitrogen and probably nitrous oxide are formed. Aq. ammonia in contact with nitric oxide produces nitrous oxide. The Badische Anilin- und Soda-fabrik found that interaction between nitric oxide and ammonia gas does not occur under ordinary conditions. P. L. Dulong found that both liquid and gaseous **nitrogen peroxide** rapidly decompose ammonia at ordinary temp., forming nitric oxide and nitrogen; and E. Soubeiran found that if the ammonia and nitrogen peroxide be dried and freed from air, the vigorous reaction furnishes nitrogen, water, and ammonium nitrite; but if traces of water and air be present, some nitrous oxide and ammonium nitrate are also formed. A. Besson and G. Rosset found that at —80° liquid ammonia reacts with solid nitrogen peroxide with explosive violence. According to P. T. Austen, a fine stream of ammonia gas in an atm. of **nitric acid** vapour burns with a yellow flame.

According to A. Bineau, **phosphorus** sublimes in ammonia gas without absorption taking place, but C. W. Böckmann, and A. Vogel said that a phosphorus amminoxide can be so prepared. F. A. Flückiger found that dry phosphorus slowly absorbs ammonia, forming a dark brittle substance; and when phosphorus is warmed with aqua ammonia, a black compound of phosphorus oxide and ammonia is produced. A. F. de Fourcroy found that when the vapour of phosphorus and ammonia are sent through a red-hot tube, phosphine and nitrogen are formed. E. C. Franklin and C. A. Kraus found liquid ammonia dissolves phosphorus only in the presence of air. H. Rose, and J. Persoz found that **phosphorus trichloride** rapidly absorbs ammonia, forming a white cloud. Much heat is developed and phosphorus amminotrichloride is formed, and this, when heated, decomposes : $5PCl_3+8NH_3=4PN_2H+15HCl+5H+P$—*vide* phosphorus trichloride. H. Rose found **phosphorus tribromide** acts in an analogous manner. C. Hugot represented the reaction with strongly cooled, liquid ammonia : $15NH_3+PBr_3=P(NH_2)_3+3NH_4(NH_3)_3Br$. Cold **phosphorus pentachloride** absorbs ammonia very slowly if at all, but if not so strongly cooled, an amminopentachloride is formed. J. von Liebig and F. Wöhler always found ammonium chloride was present, showing that some decomposition had taken place. C. Gerhardt represented the reaction by $4NH_3+PCl_5=(NH_2)_2PCl_3+2NH_4Cl$—*vide* phosphorus pentachloride. J. H. Gladstone observed the reaction occurs when the gases are moist or dry. H. Schiff represented the reaction with **phosphoryl chloride :** $POCl_3+6NH_3=(NH_2)_3PO+3NH_4Cl$. J. H. Gladstone found that at 0° the reaction is better represented by $POCl_3+2NH_3=NH_4Cl+NH_2.POCl_2$; and at 100°, $POCl_3+4NH_3=2NH_4Cl+(NH_2)_2POCl$—*vide* phosphoryl chloride. According to A. Bineau, **phosphorus trisulphide** absorbs ammonia very slowly, after 6 months' action the product had the composition $(NH_3)_2P_2S_3$. A. Baudrimont, G. Chevrier, and J. H. Gladstone and J. D. Holmes observed that **thiophosphoryl chloride** absorbs dry ammonia, forming ammines ; and H. Schiff, and G. Chevrier noted the formation of some phosphorus sulphotriamide. J. H. Gladstone and J. D. Holmes found that a dil. aq. soln. of ammonia reacts with thiophosphoryl chloride, forming thiophosphaminic acid ; and with an excess of ammonia, G. Chevrier obtained ammonium thiophosphate. A. Michaelis found that **thiophosphoryl bromide** is decomposed with difficulty by ammonia in the cold, but when heated various substances are formed—sulphur, ammonium polysulphide, ammonium phosphite, and phosphate. H. Schiff said that ammonia and **phosphorus pentoxide** furnish pyrophosphodiaminic acid, and S. Gutmann, and H. Biltz obtained a suboxide (*q.v.*). H. B. Baker showed that if the ammonia and phosphoric oxide are quite dry, no reaction occurs. T. E. Thorpe and A. E. Tutton showed that ammonia acts on a soln. of **phosphorus trioxide** in alcohol or benzene, forming a diamide and an ammonium salt of phosphorous acid. A. Stock studied the action of liquid ammonia on **phosphorus pentasulphide** (*q.v.*). Ammonia forms ammines when it reacts with the **arsenic trihalides.** A. Rosenheim and F. Jacobsohn found that **arsenic pentoxide** reacts with liquid ammonia, forming the ammine, $As_2O_5.3NH_3$; but **antimony pentoxide** does not react.

L. Clouet,[6] C. Langlois, F. Kuhlmann, and C. Weltzien found that when ammonia is passed over red-hot **carbon,** ammonium cyanide and hydrogen are formed: $2NH_3+C=NH_4CN+H_2$; some nitrogen is also formed, but, according to C. Weltzien, no hydrocarbons are produced. The production of cyanides by the action of ammonia on carbon has been investigated by E. Bergmann, and G. A. Voerkelius. H. Delbrück showed that hydrogen cyanide is produced when ammonia and carbon dioxide are passed over heated potassium. R. M. Badger gave for the equilibrium constant, $[H_2][HCN]=K[NH_3]$, in the balanced reaction : $NH_3+C=HCN+H_2$, at 800°, $K=5{\cdot}8\times10^{-6}$. A. Millot showed that when a soln. of ammonia is electrolyzed with a positive electrode of purified gas-carbon and a negative electrode of platinum, the liquid acquires a deep black colour. If this black soln. is evaporated to dryness on a water-bath, and the residue extracted with warm alcohol, a black insoluble substance is left, and a yellow soln. is obtained. When this soln. is evaporated to a syrup, it deposits a yellowish nitrogenous substance, soluble in boiling water, to which it imparts an acid reaction. The still liquid portion is evaporated repeatedly until no further deposit is obtained, and when the filtered liquid is allowed to cool it deposits crystals of carbamide. In this reaction, the synthesis of carbamide is effected by the direct action of carbonic anhydride and ammonia under the influence of the electric current. The electrolysis, during eight days, of 500 c.c. of ammonia mixed with an equal volume of water gave 6–8 grms. of the black substance and one grm. of pure carbamide. The subject has been investigated by L. Weisberg, H. von Wartenberg, and W. Bertelsmann. The formation of cyanides by the action of ammonia on the vapours of **hydrocarbons** was studied by F. Kuhlmann, D. Lance and R. L. E. de Bourgade, H. C. Woltereck, J. Mactear, P. R. de Lambilly, and C. Beindl. J. W. Beeson and J. R. Partington exploded mixtures of varying quantities of ammonia with 2 vols. of **carbon monoxide** and one vol. of oxygen at 85° and 380 mm. press. so that no steam was condensed. All the mixtures which could be ignited approximated a 95·3 per cent. decomposition of the ammonia. With some mixtures containing more than 40·5 per cent. of ammonia, the first spark did not cause explosion, a period of induction being observed, after which the propagation of the flame from the spark to the walls of the bulb was so slow that it could be followed visually. No ignition occurred in mixtures in which the ratio $NH_3/(2CO+O_2)$ exceeded 0·924. F. Kuhlmann found that under the influence of platinum black, carbon monoxide and ammonia react: $NH_3+CO=H_2O+HCN$; A. Mailhe and F. de Godon obtained an excellent yield of ammonium cyanide by using thoria as a catalyst at 410° to 450°—if alumina or zirconia is used as catalyst, a higher temp. is necessary. H. Jackson and D. N. Laurie obtained both urea and ammonium cyanate when the gases react in contact with a hot surface of platinum: $CO+NH_3=H_2+HOCN$. K. C. Bailey found that under the influence of radium emanation the second reaction occurs—the first reaction occurs only in the presence of a catalyst. The reaction was studied by G. Bredig and E. Elöd, M. Herbst, and R. K. Müller. The action of **carbon dioxide** on ammonia has been discussed in connection with the carbamates (**2**. 20, 34); the action of **carbonyl chloride** on ammonia and ammonium chloride (**5**. 39, 28); the action of carbon disulphide (**6**. 39, 42); and the action of **carbonyl sulphide** (**6**. 39, 29). K. C. Bailey observed that under the influence of radium emanation carbon dioxide and ammonia react, forming cyanate and urea. The solubility of ammonia in various carbon compounds has been discussed in the preceding section. A. B. Brown and E. E. Reid studied the alkylation of ammonia by passing mixtures of ammonia and alcohol—methyl, ethyl, η-propyl, and η-butyl—over various oxides as catalysts at 300°–500°. They found, in the order of ascending efficiency, blue oxide of tungsten, commercial silica gel, alumina, silica gel impregnated with nickel oxide, zirconia, silica gel impregnated with thoria, and a silica gel prepared by adding a sodium silicate soln. (4·5 per cent. Na_2O) to an equal volume of 10 per cent. pure hydrochloric acid. The resulting gel is broken into large fragments, suspended in running water for several days, and then dried at temp. rising in stages to 180°. For high activity, long life, and absence of side reactions, the special silica gel is much the best. The optimum temp., percentages of alcohol converted into amines, and the ratios of primary, secondary, and tertiary amines formed, using this catalyst, are as follow: methyl, 480°, 56 per cent., 5 : 12 : 3; ethyl, 465°, 39·5 per cent., 2 : 5 : 3; η-propyl, 415°, 49 per cent., 10 : 11 : 18; η-butyl, 430°, 25 per cent., 11 : 11 : 3. G. W. Dorrell studied the catalytic activity of alumina whose optimum temp. is about 300°. L. Knorr studied the action of ammonia on **ethylene oxide**; M. Knothe, on **acid dichlorides**; F. Dobler, on aromatic **aldehydes**; F. Bidet, on primary **amines**, etc. G. Baume, and A. M. Wasilieff studied the system with **methyl ether** and **ethyl alcohol** with ammonia; and C. A. Kraus and E. H. Zeitfuchs, equilibrium in liquid mixtures of ammonia and xylene. H. H. Schlubach and H. Miedel observed that ammonia or ammonium salts may act as a reducing agent on some organic compounds—phenylbutylene, styryl methyl ketone, pyridine, and nitrobenzene, but not acetophenone, benzil, benzoin, and deoxybenzoin. A soln. of sodium in liquid ammonia is added gradually to a soln. of ammonium chloride in the same solvent in which the substance to be reduced is at least partly dissolved at —80° to —50°. If the compound under investigation is not sufficiently soluble in liquid ammonia, benzene or ether may be added. In general, reduction appears to be due to the direct addition of nascent hydrogen without preliminary formation of an intermediate additive compound with the sodium. The action is highly selective and appears to resemble most closely that of sodium and alcohol. Probably owing to the low temp. of the reactions, the formation of by-products is largely avoided. The reaction was studied by A. R. Ling and D. R. Nanji, L. C. Maillard, etc., when ammonia is brought in contact with dextrose (fused or in aq. soln.), either in the form of gas or aq. soln., at a moderate temp.—say 35°–40°—combination of the ammonia with the sugar takes place. If now the liquid be heated to a higher temp., *e.g.* 100°, a vigorous exothermic reaction ensues, and dark-coloured substances are produced. Similar reactions occur when certain amino-compounds are substituted for ammonia. A. Couder found that dry ammonia acts on **cyanamide,** forming colourless soln. containing dicyanodiamide. A. B. Brown and E. E. Reid discussed the alkylation of ammonia; and H. B. Merrill, the depilatory action on calf-skins.

The acid properties of soln. of ammonium salts in liquid ammonia have been established by E. C. Franklin and co-workers.[7] According to F. W. Bergstrom, these solns. react with most of the elements above hydrogen in the electrochemical series as it is known in water. The action of the **alkali metals** and of the **alkaline earth metals** on liquid ammonia is discussed in a special section, and the effect of the gas on the heated metals is indicated in connection with the amides, or nitrides. M. Copisarow, and R. Fricke and O. Suwelaek obtained rhythmic rings of a metal hydroxide by allowing ammonia gas to diffuse into a soln. of the metal salt in gelatin. Several metals form nitrides when heated in the gas—*e.g.* **magnesium, zinc, aluminium, iron, titanium,** etc.—in other cases—*e.g.* **silver, gold, platinum,** etc.—the metal exerts a catalytic action on the decomposition of ammonia—*vide supra,* nitrides. C. van Brunt said that the circumstances of an accidental explosion indicate that during 10 years at ordinary temp. **mercury** in the safety valve of a carboy containing conc. aq. ammonia, formed a *mercury ammonium oxide.* A. F. de Fourcroy showed that many **metal oxides** are decomposed when heated in ammonia gas, forming water, nitrogen, and the metal or a lower oxide. In the case of **mercuric oxide,** nitric acid is formed. Part of the nitrogen may be oxidized to nitric oxide or nitrogen peroxide. In some cases, nitrides of the metals are formed—*e.g.* **titanium, iron, or copper oxides**—and in other cases, complex compounds containing nitrogen, hydrogen, and oxygen may be formed—*e.g.* **tungstic or mercuric oxide** (*q.v.*). R. Tupputi, and E. Fleischer found aq. ammonia decomposes **nickel sesquioxide** in the cold, forming nitrogen and nickel monoxide. A. Rosenheim and F. Jacobsohn found that with liquid ammonia **molybdic oxide** furnishes the ammine $MoO_3.3NH_3$; and **tungstic oxide** is not changed, but **tungsten dichlorodioxide** forms the ammine $WoO_3.3NH_3$. G. W. Dorrell found that ammonia is readily absorbed by alumina at 344°, but no decomposition into its elements was noticed. H. Hiendlmaier studied the effect of ammonia on various **metal hydroxides** —copper, chromium, iron, and nickel—in the presence of weak acids. According to O. Michel and E. Grandmongin, heated **sodium dioxide** reacts with dry ammonia: $2NH_3+3Na_2O_2=6NaOH+N_2$—some sodium nitrite and nitrate are also formed; **barium dioxide** acts in an analogous manner; **manganese dioxide** forms manganese sesquioxide, nitrogen and water; and **lead dioxide** forms nitrogen, and ammonium nitrite and nitrate. F. W. Bergstrom found that **molybdenum and tungsten dibromides** and **tungsten dichloride** yield slightly soluble ammoniobasic halides on treatment with liquid ammonia. **Molybdenum tribromide and pentachloride,** and **tungsten pentabromide and hexachloride,** dissolve in liquid ammonia to give red soln., the first named also giving a precipitate of ammoniobasic bromides. Dilution of the soln. yields amorphous precipitates of indefinite composition. Molybdenum pentachloride absorbs 8 mols. of ammonia gas, giving a derivative of unknown composition.

Aq. ammonia dissolves many of the heavy **metal hydroxides**—*e.g.* zinc, cadmium, cobalt, nickel, copper, and silver hydroxides; chromic hydroxide dissolves in this menstruum but sparingly; and ferrous and manganese hydroxides dissolve only in the presence of ammonium salts. The solubility is supposed to be determined by the formation of a compound of ammonia with the respective oxides. Compounds formed by the direct addition of ammonia with the oxides and salts are usually called **ammines.** The oxides of vanadium, uranium, antimony, mercury, silver, gold, and the platinum metals form solid compounds which are more or less explosive. O. Ruff and E. Geisel found that the **alkali metal hydrides** react with liquid ammonia, forming amides: $MH+NH_3=H_2+M.NH_2$. The hydrides of potassium, rubidium, and cæsium react at the m.p. of liquid ammonia —78°; sodium hydride at about —40°; and lithium hydride requires many days at ordinary temp. before it is completely transformed into amide. Many **metal salts** unite with ammonia, sometimes with the evolution of heat. For example, ammonia is absorbed by calcium chloride, zinc chloride, silver chloride, etc., forming amminochlorides. A great many complex silver ammines with the monobasic salts have been reported in which the ratio $Ag:NH_3$ is as 1 : 2, for instance, $AgI.2NH_3$; $AgClO_3.2NH_3$; $AgBrO_3.2NH_3$; $AgNO_3.2NH_3$; $AgNO_2.2NH_3$; etc. With salts of higher basicity the proportion of ammonia is greater, *e.g.* $Ag_2CrO_4.4NH_3$; $Ag_2SeO_4.4NH_3$; $Ag_2SO_4.4NH_3$; $Ag_2S_2O_7.4NH_3$; $Ag_4As_2O_4.8NH_3$; etc., are known. Some of these compounds lose ammonia on exposure to air—*e.g.* manganese amminosulphate; and lead amminoiodide—others lose ammonia when heated—*e.g.* zinc amminosulphate; calcium amminochloride; and silver amminochloride—others give off ammonium salts mixed with more or less ammonia when heated—*e.g.* nickel amminochloride; and copper amminosulphate—and some reduced metal remains behind. Some of the ammines can be volatilized unchanged—*e.g.* zinc amminochloride; and ferric amminochloride. Aq. soln. of some of these compounds are quite stable—*e.g.* cobalt and platinum ammines—and even resist the action of acids and bases; others are decomposed by water into metal salt and ammonia—*e.g.* calcium amminochloride—and others again are hydrolyzed into a sparingly soluble basic salt, hydroxide, or oxide—*e.g.* zinc amminocarbonate; thallium amminochloride; lead amminoiodide; and ferric amminochloride. K. Alberts examined the effect of heating **potassium, calcium, strontium, barium, and magnesium sulphates** in a current of ammonia. A. von Unruh studied the action of dry ammonia on **uranyl salts.**

H. P. Cady and R. Taft sought if electrolytic oxidations can occur in systems containing no oxygen, and found that with liquid ammonia as solvent, thallous iodide, cuprous iodide, hydrazobenzene, and methyl- and ethylamine hydrochlorides can be oxidized. The properties of soln. of salts, etc., in liquid ammonia were studied by F. W. Bergstrom, T. J. Webb, E. C. Franklin and C. A. Kraus, etc.

H. Tamm[8] said that aq. ammonia is oxidized by **potassium permanganate,** forming ammonium nitrate; but S. Hoogerwerff and W. A. van Dorp found that an alkaline soln. of the salt is not affected by ammonia. F. Jones represented the reaction in neutral soln. by the equation $8KMnO_4+8NH_3=4Mn_2O_3+KNO_3+KNO_2+6KOH+9H_2O+3N_2$ in agreement with the effect of phosphine, arsine, and stibine on that liquid. The reactions with permanganates in the presence of other oxides have been studied by C. F. Schönbein, J. A. Wanklyn and A. Gamgee, and S. Cloez and E. Guignet. I. M. Kolthoff said that the oxidation of ammonia by permanganate is more dependent on concentration in acidic than in alkaline soln.

According to E. J. Maumené, **ammonium oxide,** $(NH_4)_2O$, which he called **chydrazaine,** is evolved when a soln. of potassium permanganate (11 grms.) and sulphuric acid (40 grms. SO_3) is added to dried crystalline ammonium oxalate (141·2 grms.); the whole well mixed, and gently heated until it begins to boil. The gas is absorbed in hydrochloric acid, a neutral soln. of *chydrazaïne chloride,* $(NH_4)_2O.2HCl$, is formed. The crystals of the salt are readily soluble in water, but only sparingly soluble in alcohol. The sublimed salt has no water of crystallization; when an excess of a soln. of the chloride is mixed with one of platinum tetrachloride, yellow crystals of *chydrazaïne chloroplatinate,* $(NH_4)_2O.H_2PtCl_6$, are formed, but if the platinum tetrachloride be in excess, the crystals contain more chloroplatinate. The crystals of *chydrazaïne sulphate* are soluble in water and sparingly so in alcohol. *Chydrazaïne nitrate* is crystalline and an aq. soln., on evaporation, furnishes nitric acid, nitrogen, nitrogen peroxide, and *imide*, N_3H_2. None of these claims has been established.

Some reactions of analytical interest.—Ammonia is recognizable by its smell; the aq. soln. gives a blue coloration with litmus, lacmoid, and resazurin; a red colour with rosalic acid; and a brown colour with turmeric. White fumes appear when ammonia vapour is near the vapour of a volatile acid—hydrochloric or acetic acid. Ammonium salts give off ammonia when heated in contact with lime, or alkali hydroxides. An alkaline soln. of potassium iodomercurate, the so-called **Nessler's reagent,**[9] gives a brown precipitate with ammonia, and the colouring power is so great that minute traces of ammonia can be detected by its means. The reaction is also adapted to a colorimetric process for the quantitative determination of ammonia in water, etc. S. S. Graves proposed to substitute Nessler's reagent by one prepared by adding 130 c.c. of water and 100 c.c. of cold, sat. soln. of mercuric chloride to 80 grms. of sodium chloride. The mixture is shaken until the sodium chloride has dissolved, and 70 c.c. of a sat. soln. of lithium carbonate (1 per cent.) is added slowly, with shaking, so that mercuric oxide is not deposited on the sides of the flask. The soln. is usually cloudy, owing to the presence of ammonia in the substances used, but if well shaken with 3 to 5 grms. of talc powder and filtered, a clear liquid can be obtained. The soln. can be kept almost indefinitely in carefully stoppered bottles. Ammonium salts give a yellow crystalline precipitate with **hydrochloroplatinic acid,** and, unlike the corresponding precipitate with potassium salts, the precipitate on ignition leaves only platinum behind; and when the precipitate is treated with alkali-lye, ammonia is given off. According to J. L. Lassaigne, one part of ammonium chloride in 100 parts of water gives a copious precipitate; with 200 parts of water, a slight precipitate; with 400 parts of water, a very slight precipitate; and with 800 parts of water, a scanty precipitate after 12 hrs. A white precipitate of ammonium hydrotartrate, $COOH.HCOH.HCOH.COONH_4$, is produced with **tartaric acid**—the presence of sodium acetate favours the precipitation. The precipitate is soluble in alkali-lye, and mineral acids. **Sodium hydrotartrate** also gives a white precipitate with conc. soln. Potassium salts behave in an analogous manner. Unlike potassium salts, ammonium salt soln. give no precipitate with **perchloric acid**; and unlike sodium salts, no precipitate with **potassium pyroantimonate.** Both ammonium and potassium salts give precipitates with **picric acid, sodium tungstate, phosphomolybdic acid,** and **sodium nitratocobaltate.**

The ammonium salts are decomposed, with the evolution of nitrogen, when they are treated with **hypobromites,** or **hypochlorites**: $2NH_3+3NaOBr=N_2+3NaBr+3H_2O$. According to A. Trillat and M. Turchet,[10] when soln. of potassium iodide and an alkali hypochlorite are added to a liquid containing ammonia, an intense black coloration is produced due to the formation of nitrogen iodide, and as the same result is obtained when the iodine mono- or tri-chloride and an alkali are used instead of the above reagents, the reaction may be represented by the following equation: $3ClI+NH_3+3NaOH=3NaCl+NI_3+3H_2O$. In applying the test, 3 drops of a 10 per cent. soln. of potassium iodide and 2 drops of a conc. soln. of alkali hypochlorite (Eau de Javel) are added to 20 or 30 c.c. of the suspected water; the use of excess of the reagents must be avoided, as nitrogen iodide dissolves under these conditions. No compounds of nitrogen other than ammonium salts are said to form nitrogen iodide under these conditions. According to E. Riegler, if ten c.c. of the soln. to be tested is mixed with 10–15 drops of a soln. of **p-nitroaniline,** hydrochloric acid, and sodium nitrite, and a 10 per cent. soln. of sodium hydroxide be added drop by drop, the liquid becomes yellow or red if ammonia be present. According to H. Rose,[11] and J. Müller, water containing traces of ammonia colours a soln. of **mercurous nitrate** a dirty grey colour; and mercurous nitrate test-papers are coloured black by ammonia vapours. According to E. Bohlig, when a soln. of **mercuric chloride** is added to a soln. of ammonia or ammonium carbonate, white mercuric amidochloride is precipitated, and a white turbidity is produced if only

1 : 200000 is present. The presence of traces of potassium carbonate makes the reaction even more sensitive. The reaction was examined by P. Einbrodt, A. Schöyen, C. Rehsteiner, G. C. Wittstein, and A. Ferraro.

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19. The Constitution of the Ammonium Compounds and the Ammines

> A body possessing so many interesting properties as ammonia, standing as it were on the confines of mineral and of organic chemistry, and forming the connecting link between them, must even, on its own account, and still more from the remarkable variety of classes of combinations into which it enters, occupy a prominent place in the general theory of chemistry.—R. J. KANE.

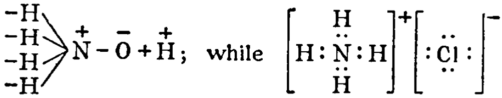
It seems as if tervalent nitrogen in ammonia, NH_3, changes into quinquevalent nitrogen in forming ammonium chloride, NH_4Cl. F. A. Kekulé[1] rigidly adhered to the doctrine of fixed valency, and the ready dissociation of ammonium chloride into ammonia and hydrogen chloride led him to assume the existence of what he designated *molecular compounds*, and to reject the hypothesis of a quinquevalent nitrogen atom in the ammonium compounds. He applied the term *atomic compounds* to those compounds in which all the atoms of the elements are united in such a way that their valencies are saturated. " These," said F. A. Kekulé, " are the true chemical molecules, and the only ones which can exist in the gaseous state." He assumed that the atoms of different molecules could attract one another so as to produce a kind of coupling of the molecules, and the coupled molecules were called molecular compounds, and symbolized accordingly thus, ammonium chloride becomes $NH_3.ClH$, etc. The nature of the atoms of the copulated molecules may be such that double decomposition is not possible, and "the two molecules, so to speak, adhere and form a group endowed with a certain amount of stability, which is always less than that of atomic combination." In other words, F. A. Kekulé assumed that molecular compounds are formed by direct addition of two or more simple mols., and the simple mols. retain to some extent their individuality, for they can be readily separated from one another apparently unchanged. F. A. Kekulé cited as examples of molecular compounds: ammonium salts, phosphorus pentachloride, iodine trichloride, crystalline salts which furnish anhydrous salt and water, etc. The compounds of silver chloride and ammonia, ferrous sulphate and nitric oxide, etc., can be added to the list. To sum up F. A. Kekulé's position: in order to make the theory of constant valency compatible with the existence of more complex molecules, it was assumed that these molecular compounds belonged to a different type of combination. These molecular compounds formed a miscellaneous group to which everything was relegated which did not fit the arbitrary hypothesis of constant valency, and it included many of the higher chlorides, higher oxides, double chlorides, hydrated compounds like the alums, etc.

The ammonia-radicle theory.—The oldest hypothesis concerning the nature of the ammonia-compounds, and that adopted by A. L. Lavoisier, supposed ammonia to be an independent base or radicle, saturating acids, and forming salts. This theory has been likened to the etherin theory of J. B. A. Dumas and P. F. G. Boullay. The radicle is NH_3; sal-ammoniac is NH_3+HCl; etc. The theory makes no attempt to explain the nature of the other classes of ammonia-compounds; nor does it explain the relation of ammonia to ordinary bases, which are metallic oxides, nor the differences between the ammoniacal salts from metallic salts of the same acid. Later on, the theory became associated with the mol. compound theory, so that sal ammoniac was represented by F. A. Kekulé as an associated complex of ammonia and hydrogen chloride, in which the ammonia remained tervalent. These compounds were considered to be analogous to double salts, and to substances with water of crystallization. This view was supported by the ready dissociation of sal ammoniac by heat—a subject discussed in connection with ammonium chloride (**2**. 20, 16). H. Rose also emphasized the analogy between compounds of ammonia and of water in various salts as exemplified by the use of the term ammonia of crystallization.

The amide theory.—In the amidogen theory of H. Davy, J. von Liebig, and R. J. Kane, ammonia is supposed to be compounded of a univalent radicle, NH_2, which he called amidogen; ammonia is regarded as *amidogen hydride,* or *hydrogen amidide or amide,* $NH_2.H$; and, added R. J. Kane, hydrogen amidide can fulfil the same functions as water—*i.e.* hydrogen hydroxide, $H.OH$—both as basic water and as water of crystallization. Sal ammoniac is hydrogen chloroamidide, $NH_2.H+HCl$; if chlorine could be abstracted from sal-ammoniac, the residue would be hydrogen subamidide as when by removing chlorine from white precipitate, mercury subamidide is formed (**4**. 31, 14). The amide theory has been likened to the acetyl theory of H. V. Regnault, and J. von Liebig.

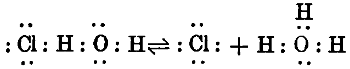
The ammonium theory.—In the ammonium theory of H. Davy, A. M. Ampère, and J. J. Berzelius, it was assumed that the ammonium compounds contain a metallic radicle, NH_4 (**4**. 31, 38), which may replace potassium, sodium, etc., in different salts. When ammonia unites with hydrogen chloride, the NH_4-radicle is formed which unites with chlorine to form ammonium chloride in the same way that potassium united with chlorine forms potassium chloride. The ammonium theory thus corresponds with the ethyl theory of J. J. Berzelius, and J. von Liebig. The nitrogen is assumed to be quinquevalent, and this is in harmony with the work of V. Meyer and M. T. Lecco, A. Ladenburg, and W. Lossen on the quaternary ammonium bases, and with the isomorphism of the ammonium and the potassium salts.

There is a difficulty in explaining the union of hydrogen chloride and ammonia on the ammonium theory: $NH_3+HCl=NH_4Cl$, because the reaction is attended by the evolution of a considerable amount of heat: $NH_{3gas}+HCl_{gas}=NH_4Cl_{solid}+42$ Cals. The separation of hydrogen chloride into its constituent elements is attended by the absorption of a considerable amount of heat—about 287 Cals.—and the union of chlorine and hydrogen with nitrogen is presumably attended by the evolution of a small amount of heat so that it might have been anticipated that the reaction would be endothermal. As M. E. Chevreul said, it is difficult to see how the feeble affinity of chlorine for nitrogen can overcome its powerful affinity for hydrogen. A. Wurtz, and L. Meyer consider the difficulty may be overcome by assuming that the affinity of chlorine for hydrogen is satisfied by the attraction it exercises in *all* the atoms of hydrogen within the molecule of ammonium chloride. H. Remy discussed the structure of the ammonium radicle; and H. Henstock gave for the electronic structure of the hydroxide:



was given by G. W. F. Holroyd for ammonium chloride. The subject was also discussed by E. B. R. Prideaux, and F. Hund. M. L. Huggins made estimates of the interatomic distances of the atoms in the ammonia molecule.

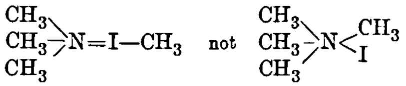
T. M. Lowry represented the strong acidity developed when, say, hydrogen chloride is mixed with water by assuming that the reaction can be symbolized $HCl+H_2O\rightleftharpoons Cl'+OH^{\cdot}{}_3$, which, expressed in terms of the electron theory of atomic structure, means that the hydrogen nucleus does not readily attach itself to an octet too fully occupied by other atoms to leave room for an additional nucleus; the water provides the required acceptor for the hydrogen nucleus, and the ionization of the acid involves the transfer of a portion from one octet to another:



$$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}:H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:H\rightleftharpoons :\overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}}: + H:\overset{\overset{H}{\cdot\cdot}}{\underset{\cdot\cdot}{O}}:H$$

meaning that the ionized acid is really an ionized oxonium salt. In the case of bases, T. M. Lowry assumes that the real function of a base is that of an acceptor of hydrogen ion. Thus, $NH_3+H^{\cdot}\rightleftharpoons NH_4$. If the base is sufficiently strong, it may not only accept the hydrogen nuclei driven from the moleules of an acid: $NH_3+H^{\cdot}\rightleftharpoons NH_4$, but it may take them from compounds like water in which they are only weakly held: $NH_3+HOH\rightleftharpoons NH^{\cdot}{}_4+OH'$, so that the strength of the base is manifested by the liberation of hydroxyl ions. Measurements of the OH'-ions show that their concentration in a soln. of ammonia in water is small; and hence ammonium hydroxide is regarded as a weak base, so weak, indeed, that there can be no question of ammonium competing with the alkali metals in basic strength. On the other hand, suppose that the salts of an unknown basic radicle were being examined, and the properties of these salts had all the properties of the ammonium salts, as R. M. Caven has pointed out, it would undoubtedly be assumed that the ammonium radicle is comparable with the alkali metals in basic strength. The physical measurements of the conc. of the OH'-ions, however, do not show whether the compound formed by ammonia and water is ionizable or not; nor whether the compound is NH_4OH, or $NH_3.H_2O$. T. M. Lowry assumes that NH_3 and not NH_4OH is the base; and that the course of the reaction is $NH_3+H^{\cdot}+OH'\rightleftharpoons NH^{\cdot}{}_4+OH'$ and not $NH_3+H_2O\rightleftharpoons NH_4OH$, followed by $NH_4OH\rightleftharpoons NH^{\cdot}{}_4+OH'$. R. M. Caven showed that both hypotheses explain equally well the properties of soln. of ammonia and of ammonium salts, whereas T. M. Lowry's hypothesis accounts for the properties of the solid ammonium salts in containing the strongly basigenic though unstable ammonium radicle. This subject was also discussed by A. E. C. Smith, H. S. C. Briggs, V. A. Izmailsky, H. Remy, T. S. Moore, etc.

H. E. Armstrong emphasized the inadequacy of the ammonium theory to account for the extraordinary stability of tetramethylammonium iodide, $(CH_3)_4NI$, towards the strongest caustic alkali, and showed that the halogen compound behaves more like an alkyl iodide than ammonium iodide. Hence, it was inferred that the halogen is not simply associated with the nitrogen, but is rather retained and protected or masked by combination with a hydrocarbon radicle. The idea can be illustrated graphically:

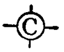


$$(CH_3)_3{\equiv}N{=}I{-}CH_3 \quad \text{not} \quad (CH_3)_3{\equiv}N{<}{}^{CH_3}_{I}$$

Following up this idea, J. C. Cain represented the ordinary ammonium salts by formulæ like $H_3N{=}Cl{-}H$ for ammonium chloride, NH_4Cl; and $H_3N{=}O{=}H_2$ for ammonium hydroxide, NH_4OH, in which tervalent halogen and quadrivalent oxygen atoms are postulated. Similarly, ammonium sulphate, $(NH_4)_2SO_4$, becomes $H_3N{=}O(H){-}SO_2{-}O(H){=}NH_3$; ammonium hydrosulphide, NH_4HS, becomes $H_3N{=}S{=}H_2$—sulphur quadrivalent; and ammonium sulphide, $(NH_4)_2S$, becomes $(H_3N){\equiv}S{=}H_2$. The ionization of ammonium salts is usually symbolized $NH_4Cl \rightleftharpoons NH^{\cdot}_4+Cl'$, and is explained, on this hypothesis, by assuming there is first a dissociation $H_3N:ClH \rightleftharpoons NH_3+HCl$, followed by an ionization of the acid, $HCl \rightleftharpoons H^{\cdot}+Cl'$, and a union of NH_3 with the hydrogen ion to form a complex $NH_3.H^{\cdot}$, thus $NH_3+H^{\cdot} \rightleftharpoons NH_3.H^{\cdot}$. There is nothing in the evidence to distinguish between $NH_4^{\cdot}$ and $NH_3.H^{\cdot}$.

The isomeric optically active substituted ammonium salts which have been reported by organic chemists are not readily explained by an ammonium theory such as has been wrongly assumed to have been established by the experiments of V. Meyer and M. T. Lecco—*vide supra.* J. C. Cain argued from the above hypothesis of the constitution of the ammonium compounds that the optical activity is the result of a similar spatial configuration as that assumed for the carbon compounds where the quadrivalent nucleus, say NCl'''', instead of quadrivalent carbon, is at the centre of a tetrahedron so that

corresponds with

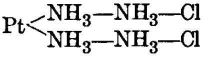


J. C. Cain similarly extends the idea to the phosphonium, $H_3P{=}ClH$; the arsonium, $H_3As{=}ClH$; the stibonium, $H_3Sb{=}ClH$; the sulphonium, $H_2S{=}ClH$; the oxonium, $H_2O{=}ClH$; and the diazonium, $C_6H_5{-}N{<}{}^{\equiv N}_{Cl}$, compounds.

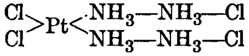
According to F. Reitzenstein, the platinum-ammonia compounds, on account of their stability and characteristic behaviour, form perhaps the best defined series among the whole of the metal-ammonia compounds, and they serve as a typical model for the study of the others. G. Magnus' observations: *Ueber einige neue Verbindungen des Platinchlorürs,* in 1828, form the starting-point of a number of important studies on the compounds of ammonia with the platinum salts—*e.g.* by J. Gros, R. J. Kane, J. Reiset, M. Peyrone, M. Raewsky, S. M. Jörgensen, A. Werner, and many others. J. J. Berzelius suggested the first theory of their constitution. He supposed they are *gepaarte Verbindungen* in which the ammonia cannot be neutralized by an acid, and is without influence on the saturation capacity of the base. The so-called J. Reiset's first chloride was symbolized $Pt.\overline{NH_2.NH_4Cl}$ by J. J. Berzelius, and this translated into modern symbols is equivalent to the formula $Cl.NH_2(NH_4).Pt.NH_2(NH_4).Cl$, where $Pt(N_2H_4)$ is supposed to be paired with $N_2H_8Cl_2$. The doctrine of union by the pairing or copulation of mols. rested on C. F. Gerhardt's *corps copulés,* and it gradually came to be identified with chemical combination (**1.** 5, 16).

C. F. Gerhardt referred the platinum bases to the ammonia type in which different atoms of hydrogen were replaced by platinum or ammonium, NH_4. The hypothesis assumed many different guises, as is illustrated by the different formulæ proposed by A. W. Hofmann, C. Weltzien, J. G. Gentele, W. Odling, H. Kolbe, H. von Euler, for any particular compound, say, J. Reiset's first chloride. C. F. Gerhardt gave $N_2H_5Pt.HCl$; A. W. Hofmann, $H_4Pt(NH_4)_2N_2Cl_2$; C. Weltzien, $N_2\{H_4(NH_4)_2Pt\}Cl_2$; W. Odling, $Pt(N_2H_5)_2.2HCl$; H. Kolbe, $[\{Pt(NH_3)_2\}H_6]N_2Cl_2$; etc. The various explanations based on the substitution of hydrogen in ammonia by ammonium was designated as " unscientific play which serves no useful purpose." The compounds concerned were also assigned systematic names consonant with the particular hypothesis employed in building their constitutional formulæ. As a result some of the longest known ammonio-metal bases and salts have half-a-dozen different systematic names. Thus, J. Reiset's first base, $Pt(OH)_2.4NH_3$, was called *platodiammonium oxyhydrate* by C. W. Blomstrand, *platodiamminihydrate* by P. T. Cleve, *diplatosamine* by C. F. Gerhardt, *ammonplatammonium oxyhydrate* by C. Grimm, *platinous tetramminohydroxide* by A. Werner. In W. Odling's system, the platinous and platinic compounds were each divided into two groups, one group contained the amine NH_2-radicle, and the other the univalent group N_2H_5, that is, $NH_2.NH_3$, called the ammonamine radicle. Thus J. Reiset's first chloride was represented $Pt(NH_2)_2.2HCl$ and M. Peyrone's chloride $Pt(N_2H_5)_2.2HCl$.

C. E. Claus, in his work *Beiträge zur Chemie der Platinmetalle* (Dorpat, 1854), rejected the ammonium theory as an explanation of the constitution of the metal-ammonias, and he advocated the older formulæ which regarded these compounds as products of the union of the metal oxide with ammonia and an acid. He was in a difficulty in explaining how the characteristic properties of ammonia are so masked that the ammonia cannot be detected by the usual reagents, and he postulated that in the ordinary ammonium compounds the ammonia is in an active state, while in the metal-ammonias it is passive. This hypothesis, said C. Weltzien, explains nothing; it can never be accepted by chemists because every atom in a compound must exercise an influence on the properties of the whole complex. C. E. Claus adopted a modified form of J. J. Berzelius's theory of copulated compounds, but instead of representing J. Reiset's first chloride, with J. J. Berzelius, as $Pt\{NH_2(NH_4)Cl\}_2$, he represented it as a compound of ammonia with platinous chloride, namely, $(NH_3)_4PtCl_2$. This view was still further modified by C. W. Blomstrand, and S. M. Jörgensen. It was assumed that ammonia molecules can unite together in chains like the dyad CH_2-groups unite in chains to form homologous series of hydrocarbons. For instance:

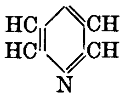


$$Pt{<}\begin{matrix}NH_3—NH_3—Cl\\NH_3—NH_3—Cl\end{matrix}$$

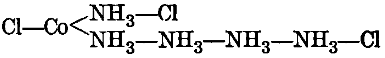


$$\begin{matrix}Cl\\Cl\end{matrix}{>}Pt{<}\begin{matrix}NH_3—NH_3—Cl\\NH_3—NH_3—Cl\end{matrix}$$

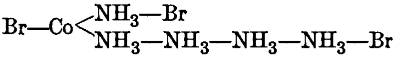
S. M. Jörgensen investigated the chloro- and the bromo-pentamminocobaltic salts, $CoCl_3.5NH_3$ and $CoBr_3.5NH_3$, and found that in each series one of the halogen atoms is related to the whole complex differently from the other two. For example, (i) One hydrogen atom remains associated with the cobalt and ammonia while the other two can be replaced by double decomposition with, say, silver nitrate; (ii) Conc. sulphuric acid displaces two halogen atoms per mol., but does not attack the third halogen atom. In order to show that one halogen atom is associated with the cobalt and ammonia differently from the other two halogen atoms, the formulæ of these compounds can be written, $(Co,Cl,5NH_3)Cl_2$ and $(Co,Br,5NH_3)Br_2$. S. M. Jörgensen further assumed that the NH_3-groups enclosed in the brackets are either united as a normal chain, $—NH_3—NH_3—$, or as a forked chain, $NH_4—NH_2<$. Pyridine, NC_5H_5, is constituted:



and can take the place of ammonia in these compounds, the resulting products are in every way analogous with the metal ammonias. If, therefore, the metal-ammonia bases are derived from NH_4 by replacing hydrogen by NH_4-groups, the substituted hydrogen atoms must be directly bound to the nitrogen atom. The existence of the pyridine compounds shows that this assumption is not necessary, and hence, S. M. Jörgensen considered it to be unlikely that the metal-ammonias contain the ammonium group. Further, in order to explain why one of the halogen atoms does not react like the other two, S. M. Jörgensen assumed that those atoms which are directly attached to the metal atom are masked and do not respond to the solicitations of chemical reagents in the normal way, while the halogen atoms which are terminal members of the ammonia chains behave quite regularly. Thus, S. M. Jörgensen represented the two cobalt salts under discussion by the formulæ:

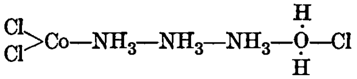


$$\mathrm{Cl{-}Co}\left\langle\begin{matrix}\mathrm{NH_3{-}Cl}\\ \mathrm{NH_3{-}NH_3{-}NH_3{-}NH_3{-}Cl}\end{matrix}\right.$$



$$\mathrm{Br{-}Co}\left\langle\begin{matrix}\mathrm{NH_3{-}Br}\\ \mathrm{NH_3{-}NH_3{-}NH_3{-}NH_3{-}Br}\end{matrix}\right.$$

and in cases where a water-molecule replaces one of ammonia, he assumed that this is linked up with the ammonia chain in virtue of the quadrivalency of oxygen. For example, the compound $CoCl_3.3NH_3.H_2O$ in which two of the halogen atoms are masked while the third behaves in the normal manner, was represented by the formula



$$\left.\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\right>\mathrm{Co{-}NH_3{-}NH_3{-}NH_3{-}}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{O}}}\mathrm{{-}Cl}$$

According to this hypothesis, the compound $PtCl_2.4NH_3$ is represented by $Pt{=}(NH_3.NH_3.Cl)_2$. The principal weakness of this view of the constitution of the ammines rests on the apparent absence of limitation to the possible number of ammonia groups which might be linked up into chains. In the great majority of cases, a metal atom can hold no more than six ammonia groups, often four, and seldom any other number. The next important contribution to this subject was made by A. Werner. The attempt to distinguish mol. from atomic compounds by structural formulæ based upon ordinary valencies deduced from the manifestations of the simple "atomic compounds," has not been successful. Some of the elements involved in the formation of the mol. compounds appear to manifest higher valencies than the numbers deduced from the simpler, more numerous, and more stable compounds. A. Werner's hypothesis seems to give a clearer insight into the constitution of double salts, complex salts, crystalline hydrates, etc., than any yet propounded; and it forms the most elegant system yet proposed for classifying large groups of complex compounds, and particularly the ammonia metal bases. Although it is fully recognized that this hypothesis has not assumed its final form, yet, as one of the fathers of philosophy has said, we begin with doubts in order that we may end with certainties; and there is the promise that the conception of mol. compounds as something specifically distinct from atomic compounds will ultimately be banished from chemistry.

Valency can be regarded as a measure of the capacity of an atom for combination with hydrogen equivalents of atoms; it is considered to be negative in combination with electropositive atoms, and positive in combination with electronegative atoms. Hypotheses have been suggested at various times, ranging from that of C. L. le Sage in 1764 to that of J. H. van't Hoff in 1881, which postulate a pre-existing force, acting in a definite direction or directions determined by the structure or rather the shape of the atom. According to C. E. Claus, the hypothesis that the valency of multivalent atoms is a pre-existing force acting with definite units of affinity is as unfounded as it is unnecessary. C. L. Berthollet recognized that there are predominant affinities in substances which are the source of their characteristic properties; and there are others which are inferior to these, but which nevertheless give rise to several remarkable phenomena. The same idea was propounded by J. Mercer, and L. Playfair. According to A. Werner, when the combining capacity of an atom, as defined empirically by the theory of valency, is exhausted, the atoms still possess a " particular kind of affinity," which enables them to form mol. complexes, corresponding with J. J. Berzelius' " compounds of higher orders " (**1.** 2, 10). S. U. Pickering, A. Wurtz, and H. E. Armstrong employed the term **residual affinity** for the affinity which remained after the ordinary valency of an element had been satisfied. In other words, **simple or primary molecules may possess a residual affinity which enables them to unite together and form more complex stable compounds.** Thus, the sulphur atom in sulphur trioxide ; the oxygen atom in water ; the chlorine atom in hydrogen chloride ; the nitrogen atom in ammonia ; the gold atom in auric chloride ; the platinum atom in platinic chloride, etc., all possess residual affinity which permits these molecules to unite additively with other molecules. The residual affinity or residual valency is not measured in terms of hydrogen equivalents, but in terms of the number of atoms bound in the molecule in excess of those which are associated by the operation of the normal exchange of valencies ; it seems to depend not on one atom alone but on the nature of all the atoms present in a particular molecule. Residual affinity appears to play a *rôle* similar to ordinary chemical affinity, but the new manifestation of valency in compounds differs from that which occurs with the radicles. For instance, **residual affinity does not lead to the combination of univalent radicles as defined by the doctrine of valency.** In illustration, water, H_2O ; antimony pentachloride, $SbCl_5$; sulphur tetrachloride, SCl_4 ; phosphorus oxychloride, $POCl_3$; phosphorus pentachloride, PCl_5 ; hydrogen cyanide, HCy ; ammonia, NH_3 ; etc. ; may be regarded as compounds in which the primary valencies of the elements are exhausted, and yet, in virtue of their residual affinity, readily form compounds like $SbCl_5.4H_2O$; $SbCl_5.3HCy$; $SbCl_5.PCl_5$; $SbCl_5.POCl_3$; etc. A. Werner draws no sharp distinctions between the union of P_2O_5 and Na_2O to form Na_3PO_4, and between $BaCl_2$ and H_2O to form $BaCl_2.2H_2O$. This does not mean that the mode of action of the two kinds of affinity is different, since both are in many ways similar. " Nevertheless," says A. Werner, " it appears at present desirable to preserve the difference because the doctrine of valency is yet in a transitional stage, and hence it is judicious to construct sharply defined concepts." A. Werner assumes that complex molecules consist of a core or inner sphere consisting of a group of atoms directly combined or coordinated by primary valencies with a central atom ; and an outer sphere or shell holding a definite number of atoms or groups of atoms in combination by the exercise of secondary valencies. The group of atoms and radicles in the inner sphere is generally represented with thin square brackets, those on the outer sphere are put outside the square brackets—*e.g.* $[PtCl_6]K_2$; $[CoF_4(OH)_2]K_2$; etc. Accordingly, A. Werner, more or less vaguely, distinguishes two kinds of valency :

1. **Chief or primary valency.**—*Hauptvalenz*—which represents those manifestations of chemical affinity which enable the combining capacities (valencies) of the elements to be expressed in terms of hydrogen atoms or their equivalents, *e.g.* Cl—, Na—, NO_2—, CH_3—, . . . The forces emanating from the central atom mainly determine the grouping of the atoms in the central core of complex compounds, although, of course, the mutual attractions of the associated atoms or radicles must be considered.

2. **Auxiliary or secondary valency.**—The conception of auxiliary valencies lies at the base of Werner's theory, but the conception is vague enough to be adaptable to requirements as particular cases arise. *Nebenvalenz*—which represents those manifestations of residual chemical affinity which are able to bring about the stable union of certain molecules as if the molecules were themselves radicles able to exist as independent molecules, *e.g.* H_2O—, NH_3—, HCl—, $CrCl_3$—, . . . The secondary valency is not to be confused with residual affinity nor with J. Thiele's partial valencies —*Partialvalenzen*—because it is determined by the mutual attractions exerted by the atoms or radicles in the central core ; these are known to possess considerable residual chemical affinity, and they have the greatest tendency to form hydrated and

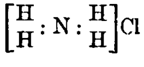
ammoniated complexes with the salts of the metals. However, there is probably no essential difference in the forces active in forming compounds exhibiting the two kinds of valency ; the actual difference is one of degree not of kind in the same sense that a millimetre differs from a metre ; or in the same way that the forces concerned with ordinary and residual affinity are the same in kind but not in quantity. Consequently, in many cases the distinction between principal and auxiliary valencies cannot be maintained.

The force concerned in the formation of compounds is supposed by A. Werner to be distributed over the surface of the atom, and to be utilized in binding a sufficient number of atoms to form an enclosing shell—A. Werner's inner sphere—about the central attracting or co-ordinating atom. When the binding capacity of an elementary atom (primary valency) appears exhausted, A. Werner assumes that the atom can still link up with other molecules (secondary valency), and build more complex molecules. There is, however, a limit to the binding capacity of both primary and secondary valencies. **The maximum number of atoms, radicles, or molecular groups—independent of their valencies—which can be directly linked or co-ordinated with a central atom is called the co-ordination number.** The co-ordination number of an atom can be determined from compounds in which the maximum number of atoms, radicles, or mol. groups, linked with a central atom, are known. The co-ordination number of most atoms, curiously enough, is six ; in many cases it is four—particularly with elements of small at. wt. like lithium, beryllium, carbon, boron, and nitrogen, or elements of high at. wt. like gold, mercury, thallium, and bismuth ; and with molybdenum and the addition products of the chlorides of the alkaline earths, the co-ordination number appears to be eight, *e.g.*

$$[Pt(NH_3)_4]Cl_2 \qquad [Co(NO_3)_6]R_3 \qquad [Ca(NH_3)_8]Cl_2$$

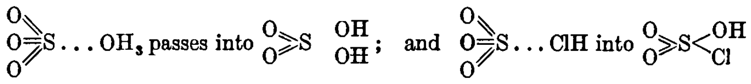
The fact that the co-ordination number for so many elements is six, and is generally independent of the nature of the co-ordinated groups, has made A. Werner suggest that the number is decided by available *space* rather than affinity, and that six is usually the maximum number which can be fitted about the central atom to form a stable system. Consequently, the co-ordination number represents a property of the atom which enables the constitution of " molecular compounds " to be referred back to actual linkings between definite atoms. A molecular compound is primarily formed through the agency of secondary valencies ; and, just as primary valencies determine the number of univalent atoms or their equivalent which can be linked to a central atom, so secondary valencies determine the number of mols. which can be attached to the central atom. The secondary valency is often active only towards definite mol. complexes, and hence the formation of additive compounds with other mol. complexes does not occur. Accordingly, the number of secondary valencies which are active towards different molecules is not always the same.

When it is desired to emphasize the distinction between primary and secondary valencies, A. Werner recommends using a continuous line for the former, and a dotted line for the latter. The nitrogen atom of ammonia, NH_3, has an unsaturated secondary valency, and the hydrogen or chlorine atom in hydrogen chloride, HCl, has likewise an unsaturated secondary valency. The formation of ammonium chloride is therefore illustrated by the scheme : $H_3N+HCl=H_3N\ .\ .\ .\ HCl$. The dotted line represents the auxiliary valency joining the hydrogen atom of HCl with the nitrogen atom of NH_3. The co-ordination number of the nitrogen atom is here 4. It is not likely that one of the hydrogen atoms in ammonium chloride is " linked with a greater amount of affinity than the other three," and very probably there is a state of equilibrium in which the affinity is distributed over all the hydrogen atoms, and a complex radicle is formed in which each of " the four atoms of hydrogen is united to the nitrogen by the same amount of affinity." Hence, A. Werner writes the structural formula of ammonium choride :

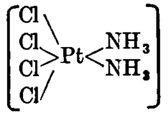

$$\left[\begin{matrix}H\\H\end{matrix}:N:\begin{matrix}H\\H\end{matrix}\right]Cl$$

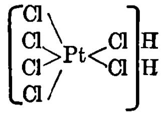
The practice of assuming an increased valency for nitrogen when ammonia unites with hydrogen chloride, says A. Werner, if consistently carried out, would make antimony tervalent in antimony trichloride, and quinquevalent in $SbCl_3.KCl$, etc. Bivalent iron in ferrous cyanide, $FeCy_2$, would become decivalent in potassium ferrocyanide, K_4FeCy_6. J. Piccard and J. H. Dardel, and P. Pfeiffer discussed this subject.

The formation of sulphuric and chlorosulphuric acids by the union of sulphur trioxide with water and hydrogen chloride respectively is brought about by the secondary valencies as indicated in the schemes: $O_3S+OH_2=O_3S \ldots OH_2$; and $O_3S+ClH=O_3S \ldots ClH$. *When one of the reacting molecules contains double-linked atoms, the auxiliary valencies may not be sufficiently strong to preserve the integrity of the new mol., and the atoms of the addition product may be rearranged.* For example, this is the case with sulphur trioxide. Thus:

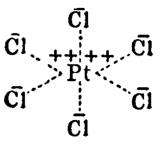


The change in the type of the compound is due to an intra-molecular rearrangement, but such a change may not occur if the secondary valency is sufficiently strong and the addition product is stable. What has been suggested appears to be applicable with the analogous reaction: $Cl_4Pt+2NH_3=Cl_4Pt \ldots (NH_3)_2$; and $Cl_4Pt+2KCl=Cl_4Pt \ldots (ClK)_2$. A. Werner represents the two latter compounds by the respective formulæ: $[Pt(NH_3)_2Cl_4]$, and $[PtCl_6]K_2$. All four chlorine atoms can be removed from the first compound without disturbing the ammonia mols., and consequently the chlorine atoms do not act as intermediate links binding the NH_3 mols. to the platinum, as they would in, say, $Cl_2Pt(Cl.NH_3)_2$. It is therefore inferred that the NH_3 mols. are directly attached to the platinum atom. Again, no difference has been detected in the chemical behaviour of the four chlorine atoms. This would not be the case if the two ammonia molecules were intermediate links between two of the chlorine atoms, and the central atom of platinum, as would be the case in, say $Cl_2Pt(NH_3.Cl)_2$. Hence, in all probability, the six groups are all attached directly to the platinum. Consequently, A. Werner writes:

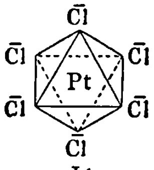




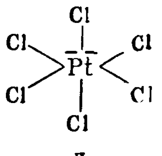
The latter formula has been established in a manner similar to the former. A. Werner assumes that four of the chlorine atoms are attached to platinum by principal valencies, and two by auxiliary valencies; and that the last two chlorine atoms are not saturated so that the hydrogen atoms may attach themselves at these points. T. M. Lowry modified the idea by assuming that the quadrivalent platinum atom begins by attracting to itself a shell of six chlorine ions as in I*a* of the following schemes where the electrostatic attractions or electrovalencies are represented by dotted lines. The orientation of these six ions is identical with that of the six chlorine ions distributed about each ion of sodium in a crystal of sodium chloride—I*b*. The outer shell



I*a*



I*b*



II

of 32 electrons is completed by drawing a pair of electrons from each of the six chlorine ions. These six duplicates are held in common by platinum and chlorine, each element claiming an equal share. The platinum therefore gains six electrons, and each chlorine atom loses one. The result of this transfer is illustrated above by formula II. The bivalent ion, $PtCl_6$, so formed contains six neutral chlorine atoms held by co-valencies, and the double negative charge is held by the atom of platinum. The platinum atom is entirely surrounded by chlorine, and in the non-ionized potassium salt, the orientation of the two potassium atoms is determined by crystallographic considerations of close-packing. The electronic structure was discussed by L. C. Jackson, D. M. Bose, L. A. Welo and A. Baudisch, N. V. Sidgwick, and B. Cabrera.

A study of the platinum-ammines shows that a large number of them can be arranged in two well-defined series. One series is derived from platinic chloride, $PtCl_4$; and the other from platinous chloride, $PtCl_2$. The co-ordination number of the former is six; and the latter, four. Thus, with ammonia and chlorine as the acidic radicle in the complex,

I. *Platinum-ammines derived from platinous chloride*—$PtCl_2$.

	Werner's formula.	Old formula.
1. Tetrammineplatinous chloride . . .	$[Pt(NH_3)_4]Cl_2$	$PtCl_2.4NH_3$
2. Chlorotriammineplatinous chloride . . .	$[Pt(NH_3)_3Cl]Cl$	$PtCl_2.3NH_3$
3. Dichlorodiammineplatinum (two isomers) . .	$[Pt(NH_3)_2Cl_2]$	$PtCl_2.2NH_3$
4. Potassium trichloroammineplatinite . . .	$[Pt(NH_3)Cl_3]K$	$PtCl_2.KCl.NH_3$
5. Potassium tetrachloroplatinite. . .	$[PtCl_4]K_2$	$PtCl_2.2KCl$

II. *Platinum-ammines derived from platinic chloride*—$PtCl_4$.

1. Hexammineplatinic chloride	$[Pt(NH_3)_6]Cl_4$	$PtCl_4.6NH_3$
2. Chloropentammineplatinic chloride . .	$[Pt(NH_3)_5Cl]Cl_3$	$PtCl_4.5NH_3$
3. Dichlorotetrammineplatinic chloride . .	$[Pt(NH_3)_4Cl_2]Cl_2$	$PtCl_4.4NH_3$
4. Trichlorotriammineplatinic chloride . . .	$[Pt(NH_3)_3Cl_3]Cl$	$PtCl_4.3NH_3$
5. Tetrachlorodiammineplatinum (two isomers) .	$[Pt(NH_3)_2Cl_4]$	$PtCl_4.2NH_3$
6. Potassium pentachloroammineplatinate . .	$[Pt(NH_3)Cl_5]K$	$PtCl_4.KCl.NH_3$
7. Potassium hexachloroplatinate . . .	$[PtCl_6]K_2$	$PtCl_4.2KCl$

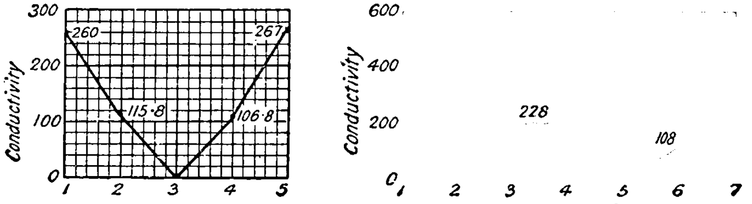
The simple or compound radicles which form the complex represented within the square brackets, are supposed to be directly united with the central atom of platinum. The complex takes part in chemical reactions as if it were one individual radicle. The substituted ammonias, methylamine, propylamine, water, hydroxylamine, pyridine—symbolized *py*—aniline, toluidine, ethylenediamine, $NH_2.CH_2.CH_2.NH_2$—symbolized *en*—phosphine, arsine, stilbine, mercaptan, etc. can take the place and function like ammonia without altering the type. The substitution may be partial or complete. In the case of hydroxylamine, the reducing action prevents the formation of platinic salts, and only the platinous salts have been made—*e.g.* $[Pt(NH_2OH)_4]Cl_2$; $[Pt(NH_3)_2(NH_2OH)_2]Cl_2$; $[Pt(NH_2OH)_2Cl_2]$; etc. In the case of ethylenediamine, one molecule replaces two molecules of ammonia. The acidic radicle in the complex can be replaced by acidic radicles—Cl, Br, NO_3, CO_3, SO_4, OH, Cy, SCy, etc.; and if the basic radicle ammonia or its eq. in the complex is replaced by an acidic group, the complex becomes acidic instead of basic and the platinic ammine complexes finally pass from electro-negative (basic) radicles to electropositive (acidic) radicles. Potassium chloroplatinate is the end-member of the series of platinic ammines and potassium chloroplatinite is the terminal member of the series of platinous ammines. It will be obvious that an enormous number of derivatives are conceivable.

Nomenclature of the metal ammines.—For a long time, the complex metal ammonia compounds were named after the discoverer or an investigator of the salt, or after some distinctive peculiarity, generally the colour—luteo—from *luteus*, brownish or orange-yellow; rosao—from *rosa*, rose-red; purpureo—from *purpura*, purple; praseo—from *πράσιος*, leek-green; flaveo—from *flavus*, golden-yellow; croceo—from *κρόκος*, saffron; xantho

—from ξανθός, yellow; violeo—from *viola*, violet; rhodeo—from ῥόδον, the rose. A. Werner's system of naming the metal-ammonia compounds has been almost universally adopted. The constituents of the complex are taken first; and of these, the acid radicles with the suffix "o" come first; then follow any groups which behave like ammonia, *e.g.* H_2O is called **aquo**; O.NO, **nitrito**, or NO_2, **nitro**; NO_3, **nitrato**; CO_3, **carbonato**; SO_3, **sulphito**; SO_4, **sulphato**; SCy, **thiocyanato**; etc. And lastly, preceding the metal itself, each ammonia molecule is designated an **ammine**, spelt with a double "m" to distinguish the word from the amines or substituted ammonias. The prefixes di, tri, . . . indicate the number of each. The whole is written as one word. Examples appear in the above list. T. Steche made some remarks on the nomenclature of A. Werner's system.

The valency of the complex is numerically equal to the difference between the ordinary valency of the central atom and the number of negative (acidic) elements or groups attached to the metal. Thus, the normal valency of platinum in the first of the above series is 4, hence the valency of $[Pt(NH_3)_5Cl]$, with one negative (acidic) group "Cl," will be 3; this means that the complex in question acts as a tervalent electropositive (basic) radicle; and it can unite with three univalent electronegative (acidic) radicles. The valency of $[Pt(NH_3)Cl_5]$ with five negative (acidic) groups, "Cl," will be —1. This means that the complex under consideration will act as a univalent electro-negative (acidic) radicle, and it can accordingly unite with one electropositive (basic) radicle like potassium, sodium, etc. If the valency of the acidic radicles in the complex is numerically equal to the normal valency of the central atom, the complex will be nullvalent. This is the case, for instance, with the complex $[Pt(NH_3)_2Cl_4]$.

The nullvalent ammine bases are non-electrolytes, they do not conduct electricity. In the other ammine bases the complex forms one ion which is either electropositive (basic), and therefore a cation, or else electronegative (acidic), and therefore an anion. During electrolysis, the components of the complex are not disturbed. The mol. conductivities of the ammine derivatives of $PtCl_2$ at 1000 litres dilution are indicated in Fig. 42; the conductivities of the derivatives of $PtCl_4$ are indicated in Fig. 43; the second derivative, $[Pt(NH_3)_5Cl]Cl_3$, is not known. The electrical conductivities of these compounds correspond with the ions obtained on electrolysis, as indicated by the formulæ in the above tables. The hydroxides are strong bases and in that respect resemble the caustic alkalies, for when boiled with ammonium salts they expel ammonia; they absorb carbon dioxide from the air to form carbonates or carbonato-compounds; they precipitate the hydroxides of aluminium, iron, etc., from solns. of their salts; and in the case of aluminium, the hydroxide is soluble in an excess of the base as is the case with caustic alkalies. The ammonia groups in the ammines are not attached in the "loose" way typified by the so-called ammonia of crystallization, but they are bound so firmly and intimately as to produce a complete change in the character of the salts. For example, the platinum is not precipitated from soln. of the ammines as sulphide by hydrogen sulphide; the ammonia is not expelled by potash or by chlorine; and the chlorine, presumably in the complex, is not precipitated by silver nitrate. As a matter of fact, the analytical reactions of each base are characteristic of the complex as a whole, and of the radicles associated with the complex—indicated outside

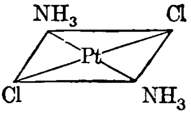


Platinochloroammines. Platinichloroammines.

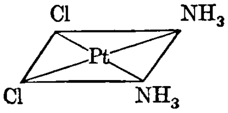
FIGS. 42 and 43.—The Electrical Conductivities of the Platinumchlorammine Derivatives. (The abscissæ refer to the numbers in the above tables.)

the square brackets in the above formulæ. Thus, with the cobalt ammines, cobalt tervalent, all the bromine in $[Co(NH_3)_6]Br_3$ is precipitated by silver nitrate; in $[Co(NH_3)_5Br]Br_2$ only two-thirds of the total bromine is precipitated by silver nitrate; in $[Co(NH_3)_4Br_2]Br$, only one-third of the total bromine is precipitated; and in $[Co(NH_3)Br_3]$ none of the bromine is precipitated.

M. Peyrone, and P. T. Cleve showed that there are two isomeric platinous diamminodichlorides; C. W. Blomstrand, P. T. Cleve, and S. M. Jörgensen consider that the difference can be represented graphically by $Cl.Pt.NH_3.NH_3.Cl$, and $Cl.NH_3.Pt.NH_3.Cl$. A. Werner believes that the isomerism is due to a difference in the spatial arrangement of the four radicles. If the four radicles be attached to a central platinum atom as if they were at the angular points of a regular tetrahedron, isomerism could not be expected because the four groups can be interchanged without altering their relations with one another. Hence it is inferred that the groups are arranged about the central atom of platinum in one plane. The resulting isomerism can be graphically illustrated by the schemes:

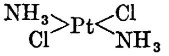


Trans-position.



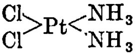
Cis-position.

or by the more usual type of formulæ:



$$\begin{matrix}NH_3\\Cl\end{matrix}>Pt<\begin{matrix}Cl\\NH_3\end{matrix}$$

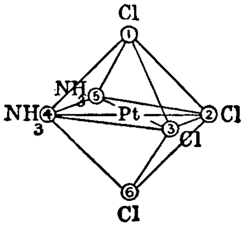
Trans-platinodichlorodiammine.



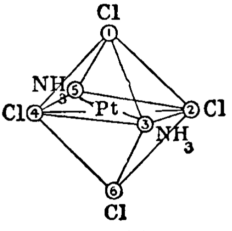
$$\begin{matrix}Cl\\Cl\end{matrix}>Pt<\begin{matrix}NH_3\\NH_3\end{matrix}$$

Cis-platinodichlorodiammine.

With platinic compounds having a co-ordination number 6, the six co-ordinated units in the complex appear to adopt some symmetrical arrangement, and to behave as if they were located at the six vertices of an imaginary regular octahedron described about the sphere of influence of the central atom. Thus, the two isomers of $[Pt(NH_3)_2Cl_4]$ can be represented by:



Cis-position.



Trans-position.

If the corners of the octahedral figure be always numbered 1 to 6 as shown in the diagram, the relative positions of the acidic or basic radicles can be indicated by numbers. Assuming that the diagrams correctly represent the relative position of the radicles, the cis-compound is called the 2·3-tetrachlorodiammineplatinum, and the trans-compound the 2·4-tetrachlorodiammineplatinum. The geometry of co-ordination was studied by R. Straubel, and G. F. Hüttig.

R. Abegg and C. Bodländer suggest that the stability of a complex depends upon the so-called electro-affinity of the ions, *i.e.* on the affinity of the radicles for electric charges or electrons. This can be approximately measured in terms of the electrolytic potential, on assumption that the unknown conc. of the free atoms in sat. soln. are the same for all elements. In a general way, the smaller the numerical value of the electrolytic potential (positive or negative) of a salt, the greater the tendency to form complex ions. In the further development of their theory, R. Abegg and G. Bodländer distinguish between what is called the atom or radicle affinity and electro-affinity. The stability of inorganic compounds depends not so much on the affinity of the atoms or radicles for one another as upon their affinity for electric charges. Sodium chloride, for instance, is said to be a stable compound, not so much because of the strong affinity between the atoms of chlorine and sodium as because a great deal of free energy must be expended in order to resolve the compound back into its elements—or, electrochemically speaking, to discharge the $Na^{\cdot}$ and Cl' ions. When the atom affinity between the two components of a compound is feeble, ionization can occur without the expenditure of much energy. On the other hand, salts like the mercury cyanide and halides are but little ionized in soln. because it is assumed the affinity of the atoms for one another is large enough to prevent much ionization. The electro-affinity of an ion for its charge is a constant, the atom affinity depends upon the particular elements in combination. Compounds formed by the union of elements with strong atom affinities have a tendency to form complex anions—*e.g.* $[HgI_4]''$, $[PtCl_6]''$, $[AuCl_3]'$, etc. In the formation of what A. Werner calls *Einlagerungscomplexe* or penetration complexes in a reaction of the type $MX_m+nA \rightarrow [MA_n]X_m$, where n is the co-ordination number of the metal, the anion X must, in general, be relatively feebly connected with the complex in what A. Werner calls the *zweite Sphäre*—the second or outer sphere—so that a great atom affinity between X and M would hinder the formation of such a complex cation but favour the formation of a complex anion.

It is not to be supposed that the heat of combination (meaning the free energy of combination) of two elements is a measure of their atom affinities. A difference in the composition of a series of solid salts (of the stronger acids) is often attended by eq. differences in the heats of formation so that the heat of formation appears to be an additive property. In the simplest cases (*e.g.* the halides), the heat of formation is the sum of contributions made by each component. Neglecting the small heats of ionization and solution, the heat of combination of simple salts will be the sum of the electro-affinities of each of the two ion-forming components, plus the atom affinity of the component elements ; and with complexes, yet a fourth term, the heat of formation of the uncharged complex must be added. Consequently, the strength of the union between two elements is not measured by the heat of combination alone. Often, indeed, the heat of combination of the elements with a relatively large affinity for one another is small. This is the case with compounds of the noble metals and their neighbours in the electrochemical series. For example, the behaviour of gold bromide on ionization suggests that the elements have a strong affinity for one another, whereas this salt readily gives off bromine when warmed, presumably because the heat of formation is small—nearly 9 Cals.

The thermal phenomena of neutralization and double decomposition are abnormal if a complex anion is formed. Abnormal heats of neutralization or deviations from the law of thermo-neutrality are characteristic of compounds with a high atom affinity. The halides of copper, silver, gold, cadmium, mercury, and platinum have small or anomalous ionization constants, and abnormal heats of formation. The heats of precipitation (the negative values of heats of soln.) of sparingly soluble, chemically analogous compounds were shown by J. Thomsen to be greater the less the solubility of the salt. A large heat of precipitation means that the heat of formation of the solids is relatively large. A low solubility may be regarded as a consequence of small ionization, and the two properties run parallel with sparingly soluble substances. Examples are thallous chloride, silver and lead halides, etc. The thermal data with the halogen (excepting fluorine), sulphur, nitrogen, and carbon compounds of gold correspond with a relatively large atom affinity so that salts of the halogen acids, thiosulphuric, sulphurous, thiocyanic, and hydrocyanic acids can exist in aq. soln. Salts of the oxygen acids—sulphates and nitrates—are almost completely hydrolyzed in aq. soln. The halides are protected from the same fate by the formation of complex anions, $[AuCl_4]'$.

$[AuCl_3OH]'$, etc.—the linkage between the metal and the acid radicle is not broken and virtually no gold ions are formed. If auric tetramminonitrate, $[Au(NH_3)_4](NO_3)_3$, be treated with potassium chloride, auric tetramminochloride, $[Au(NH_3)_4]Cl_3$, is probably first formed and, owing to the affinity between the outer sphere and the complex itself, ammonia is displaced and the series of auric amines, $[AuCl(NH_3)_3]Cl_2$, $[AuCl_2(NH_3)_2]Cl$, and $[AuCl_3NH_3]$, is produced. As a matter of fact, some of the combined chlorine passes out with the ammonia as ammonium chloride, and hydroxyl remains in the complex. This subject has been studied by F. Ephraim, A. Pieroni, E. Weitz, etc.

F. Ephraim found that about 80 per cent. of the 167 ammino-compounds he examined had the co-ordination numbers 2, 4, 6, and 8. The ammino-compounds fall into various classes according as the anion is included in the complex—the mol. ammines—or the cation is included in the complex; there are also the so-called double-shell ammines; the mixed compounds, etc. Comparing the physical properties of the ammines of the halides, it follows that (i) in the group of the alkali and alkaline-earth metals and magnesium, the affinities in the formation of the higher ammoniates are smaller the greater are the weight, at. vol., and electrolytic potential of the metal-ion, the more strongly negative and the smaller is the anion, and the greater the heat of formation and vol. concentration in formation of the salt. (ii) The iron group obeys the same rules, but the effects of the weight of the cation and vol. contraction are reversed. (iii) The copper, zinc, and lead compounds obey the same rule in some cases, but in others inverse rules. (iv) High m.p. and low solubility of the ammonia-free salt influence the stability of the ammoniates. The lattice structure derived from the X-radiograms indicates that in the hexammine-compounds of the halides of the iron metals, manganese, and zinc, the ammonia molecules are very closely packed, there being practically no free space in the metal-hexammine complex; the calculated spaces occupied by the halogen atoms are in agreement with those observed for normal polar binary compounds. The formation of the ammonia compound is in these cases accompanied by a separation of the metal from the halogen-ion, involving mechanical work, E, which may be calculated. The total heat of formation of the ammoniate involves this value, E, and the energy concerned in the association of the ammonia mols. with the cation, where E is small, *i.e.* where the cation and anion are already somewhat separated, as in the iodides, the ammoniate will be more stable for the same cation. The differences in affinity in the formation of the ammoniates are therefore bound up with space considerations; the instability of the ammoniates of the alkali metals, for example, depends not so much on the low energy involved in association of the cation with ammonia mols. as on the high value of E.

Crystalline magnesium chloride, $MgCl_2.6H_2O$, is represented, according to A. Werner's scheme, by the formula $[Mg(OH_2)_6]Cl_2$, and similarly with the other salts crystallizing with six mols. of water. A. Werner thinks that the alums $KAl(SO_4)_2.12H_2O$, and other hydrates with an abnormally large proportion of water, owe their existence to the addition of polymerized mols. of water; $(H_2O)_2$, or H_4O_2, is then attached as one mol. to the central aluminium atom, and alum becomes $[Al(H_4O_2)_6](SO_4)_2K$. With these sulphates, A. Werner considers that one mol. of the water is attached to the sulphate residue: $Zn(H_2SO_4)6H_2O$, or $[Zn(H_2O)_6]H_2SO_4$, in agreement with the great difficulty involved in driving off the last mol. of water, and with the fact that both potassium and ammonium sulphates are anhydrous, and when introduced into a sulphate with seven mols. of water, the resulting double salt crystallizes with six. The water of crystallization is thus a source of difficulty with the co-ordination theory. Hence, in studying the hydrates, it is necessary to distinguish between acidic and basic water. Many of the hydrates have not yet been studied in the light of A. Werner's hypothesis. The subject was discussed by H. T. F. Rhodes,[2] and J. M. Brown.

It may be added that A. Werner's theory furnishes an interesting explanation of the apparent isomorphism of such pairs of compounds as $K_2SnCl_4.2H_2O$

and $K_2FeCl_5.H_2O$; $MnCl_2.4H_2O$ and $BeNa_2F_4$, which can be respectively formulated:

$$[SnCl_4(H_2O)_2]K_2 \qquad [FeCl_5.H_2O]K_2 \qquad [Mn(H_2O)_4]Cl_2 \qquad [BeF_4]Na_2$$

This shows that these pairs of compounds have a similar constitution in spite of the apparent dissimilarity exhibited by the ordinary chemical formulæ. The general subject has been discussed by:

A. Werner, *Neuere Anschauungen auf dem Gebicte der anorganischen Chemie*, Braunschweig, 1913; London, 1911; B. Schwarz, *Chemie der anorganischen Komplexverbindungen*, Berlin, 1920; London, 1923; and J. D. M. Smith, *Chemistry and Atomic Structure*, London, 1924.

N. Bohr [3] discussed the fitness of configurations of the electrons in various atoms for the formation of ions. N. V. Sidgwick has extended Bohr's theory to the electronic structure of atoms in co-ordination compounds. The subject was also discussed by J. D. M. Smith, and others at the Faraday Society's discussion on *The Electronic Theory of Valency*. A. Job discussed the catalyzed reaction $NH_3+HCl=NH_4Cl$ on the assumption that an unstable electronic system is formed as an intermediate product.

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§ 20. The Metal Ammines, or Metalammoniates

T. Weyl[1] showed that sodium and potassium, and G. Gore that sodium, are soluble in liquid ammonia; C. A. Seely observed that these elements, as well as lithium and rubidium, are soluble in that menstruum; and H. Moissan studied soln. of rubidium and cæsium in liquid ammonia. Conc. soln. are copper-red, and have a bronze lustre, but dil. soln. are blue. The blue colour of the soln. recalls the blue-coloured halide salts of potassium and sodium; and the blue-coloured soln. of the alkali metals in the fused amide observed by A. W. Titherley. The colour of the soln. differs but slightly for different metals, although the appearance of yellow tints is noticeable in the case of calcium. More dil. soln., beginning at about 2 or 3 times normal, show no metallic lustre, but possess a very characteristic deep blue colour. In thin films, the conc. soln. likewise appear blue in transmitted light; but even for the blue rays the absorption is very great. A soln. of sodium in ammonia containing 0·004 gram-atom of metal per litre, just allows the filament of a 16-candle-power lamp to be distinguished through a thickness of 1 cm. The absorptive power of potassium in ammonia is practically identical with that of sodium. W. Palmaer, and C. A. Kraus also obtained blue soln. by electrolyzing liquid ammonia soln. of tetraalkyl ammonium salts. The methyl, ethyl, and propyl salts give blue soln., but not the amyl salt. The blue colour is ascribed to the presence of the free electropositive group NR_4—*vide* ammonium amalgam, **4**. 31, 38. According to O. Ruff and E. Geisel, 100 mols of liquid ammonia dissolve 21·1 gram-atoms of potassium at 0°; 20·9, at —50°; and 20·7, at —100°. The solubility thus increases slightly with rise of temp. Similarly, 100 mols of liquid ammonia dissolves 16·3 gram-atoms of sodium at 22°; 17·03, at 0°; 18·1, at —30°; 18·55, at —50°; 19·23, at —70°; and 20·1, at —105°. The solubility thus decreases with rise of temp. With lithium, 100 mols. of liquid ammonia dissolve 25·4 gram-atoms of the metal at all temp. between 0° and —80°. Lithium was found by C. A. Kraus to be soluble in ethylamine, but less so in methylamine, and insoluble in propylamine. Potassium dissolves rather slowly in ethylenediamine. Sodium and potassium are insoluble in ethylamine, and, according to H. Moissan, insoluble in methylamine free from ammonia. C. A. Kraus also found lithium, sodium, and potassium to be insoluble in secondary and tertiary amines.

O. Ruff made soln. of potassium by the electrolysis of a soln. of potassium iodide in liquid ammonia, when the substance collects on the negative pole in copper-red drops. T. Weyl supposed that the blue soln. which he prepared contained veritable compounds analogous to ammonium, NH_4, but with a hydrogen atom replaced by one of the alkali metal. Hence the names **potassammonium,** NH_3K, and **sodammonium,** NH_3Na. C. A. Seely supposed the liquids to be simple soln. of the alkali metals in liquid ammonia. T. Weyl, and J. A. Joannis regarded them as soln. of compounds of the alkali metal and ammonia in the solvent ammonia. The evaporation of the soln. in air, said J. A. Joannis, furnishes a deep copper-red solid whose analysis corresponds with KNH_3; but O. Ruff and J. Zedner said that it is purely chance that the proportions J. A. Joannis found were 1 : 1. He gave for the heat of formation, $NH_{3gas}+K_{solid}=KNH_{3solid}+6{\cdot}3$Cals., or, $NH_{3liq.}+K_{solid}=KNH_3+1{\cdot}9$ Cals.; and $NH_{3gas}+Na_{solid}=NaNH_{3solid}+5{\cdot}2$ Cals., or, $NH_{3liq.}+Na_{solid}=NaNH_3+0{\cdot}8$ Cal. H. Moissan said that the temp. of dissociation of potassammonium at ordinary press., is —2°. C. A. Kraus and W. W. Lucasse found that the composition of the liquid phase of sodium in the presence of liquid ammonia is :

	−51·6°	−42·5°	−46·4°	−47·4°	−51·9°	−55·9°	−59·7°
Molar per cent. Na	7·09	4·97	2·64	6·27	2·09	1·81	1·62

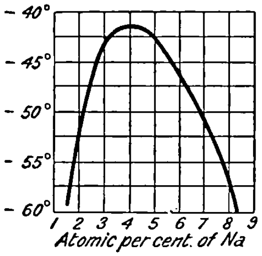

FIG. 44.—Solubility of Sodium in Liquid Ammonia.

The results are plotted in Fig. 44. H. P. Cady found the electrical conductivity is not electrolytic, but the conc. soln. behaves like a metal conductor, whose conductivity increases the greater the proportion of alkali metal in soln. Observations were made by E. Legrand; and M. Ascoli found that ammonia moves against the current through a plug of alumina, but if sodium be present, the direction is reversed. C. A. Kraus said that the conduction in liquid ammonia is ionic. The metal constitutes the positive ion and is identical with the positive ion of a salt of the metal dissolved in ammonia. The negative ion constitutes a new species of anion. It is supposed to consist of a negative charge, an electron, surrounded by an envelope of solvent mols. The electron is thus in equilibrium with ammonia according to the equation $\ominus(NH_3)_n\rightleftharpoons\ominus+nNH_3$; and at the same time, the electron is in equilibrium with metal cations and neutral metal atoms: $M^{\cdot}+\ominus\rightleftharpoons M$. J. A. Joannis said that the mol. wt. by vap. press. and f.p. methods correspond with the doubled formulæ, $NaH_3N.NH_3Na$, and $KH_3N.NH_3.K$. G. E. Gibson and T. E. Phipps measured the conductivity of soln. of the alkali metals in liquid ammonia and in methylamine. E. C. Franklin and C. A. Kraus determined the mol. wt. of sodium and lithium in liquid ammonia by the b.p. method; and C. A. Kraus, by the vap. press. method. The changes of press. with soln. more conc. than $0{\cdot}1N$, are smaller than those represented by the usual vap. press. law; this is due to the tendency of the soln. to separate into two phases for which the critical point is 3 molar per cent. of metal. O. Ruff and J. Zedner found the b.p. curves of liquid ammonia soln. of lithium, sodium, potassium are of the usual type at small conc., but with more than 8 at. per cent. of the metal, the curves begin to rise rapidly, indicating the possible existence of true compounds. With sodium, above —46°, one liquid phase exists at any conc., but below this temp. two liquid phases or one solid and one liquid phase are present. There is a eutectic at —111° on the f.p. curve corresponding with Na : $5NH_3$. C. A. Kraus and co-workers measured the sp. gr. of the soln. O. Ruff and J. Zedner gave for the b.p. of soln. in liquid ammonia :

	Li			Na			K		
At. per cent.	2·31	5·74	11·83	0·91	5·23	11·16	0·73	2·36	5·54
B.p.	−33·1°	−32·7°	−29·5°	−33·33°	−33·1°	−30·5°	−33·2°	−33·0°	−32·5°
Mol. wt.	10·9	12·3	4·9	36·2	75·4	20·1	74·8	64·0	67·9

for the f.p. of these soln. :

	Li			Na			K		
At. per cent.	6·8	9·9	15·6	2·3	8·3	15·9	2·0	5·9	12·0
F.p. I.	−77°	−77·5°	--79°	−77°	−78°	−81°	−76°	−78°	−83°
F.p. II.	—	—	—	−115°	−109°	−111°	—	—	—

and for the temp. of complete miscibility of the two phases with sodammonium :

At per cent. Na	0·5	0·8	1·4	2·8	5·9	8·3	12·9
Temp.	miscible		−50°	−47°	−54°	−61°	−72°

C. A. Kraus and W. W. Lucasse measured the electrical resistance of soln. of potassium and sodium in liquid ammonia.

The blue soln. of the alkali metals in ammonia gradually decompose into the metal amide and hydrogen : $2NaNH_3=2NaNH_2+H_2$. C. A. Kraus found that the stabilities of the soln. increase approximately in the order : potassium, calcium, lithium, and sodium. O. Ruff and E. Geisel found that at room temp. the soln. of potassammonium decomposes in two or three days $KNH_3=KNH_2+H$; and at higher temp., the decomposition is faster ; and at −60° in the presence of platinized asbestos, the soln. is decomposed in a few hours. The decomposition of rubidammonium occurs in 6–10 hrs. at ordinary temp. ; cæsammonium, in 1–2 hrs. ; lithammonium, and sodammonium, in 2–3 weeks. There is no evidence of the formation of a definite compound on the vap. press. curves, Fig. 45. J. A. Joannis, and E. C. Franklin found that the reaction, however, is catalyzed by metal oxides, hydroxides, etc. The temp. at which the alkali metals are attacked by ammonia vapour at atm. press. were found by H. Moissan to be lithium, 70° ; sodium, −20° ; potassium, −2° ; rubidium, −3° ; cæsium, 40° ; and calcium, 20°. Solid ammonia at −80° has no action on these metals. The decomposition of the soln. is more rapid in light than in darkness, and J. A. Joannis found that the rate at which hydrogen is evolved in a sealed tube decreases with time. He attributed this to the influence of the increasing hydrogen press. on the rate of the reaction, but C. A. Kraus found no evidence of a decrease in the rate of the reaction by increasing the conc. of the hydrogen. There is a steady increase in the velocity of the reaction up to a constant rate. The acceleration is attributed to the catalytic influence of sodamide. The rate of evolution of hydrogen finally slackens as the reacting constituents are consumed. According to J. A. Joannis, if a slow current of *oxygen* be passed through the soln., the liquid becomes bluish-black, then blue, and finally colourless. A gelatinous precipitate is formed whose composition approximates **sodium amminomonoxide,** $Na_2O.NH_3$. This substance dissolves in water with the evolution of much heat, but no gas is formed. T. Weyl likewise obtained **potassium diamminomonoxide,** $K_2O.2NH_3$; with a more protracted contact, the higher alkali oxides are formed. According to H. Schrader, the amides of the alkali metals undergo autoxidation, with the formation of nitrite, hydroxide, and ammonia. When finely-divided sodamide is exposed to air in presence of a little water, a yellowish-red oxidation product is formed, which is a peroxide, probably of the formula $NaNH_2O_2$. A sample of sodamide gave in fifty-eight days at ordinary temp. 0·44 mol. per cent. peroxide and 6·9 per cent. nitrite. In dry air, autoxidation does not take place at the ordinary temp., but at 100° to 110° the peroxide is slowly formed. The peroxide is stable in dry air, but in moist air is changed into a white substance, the aq. soln. of which gives the peroxide reaction. C. Hugot found that *sulphur* forms a sulphide ; *selenium,* a selenide ; and *tellurium,* a telluride. J. A. Joannis said that *nitrogen* has no action ; *nitrous oxide* reacts : $N_2O+2KNH_3=KNH_2+NH_3+KOH+N_2$; and with a longer action : $N_2O+2KNH_3=KN_3+KOH+2NH_3$; and *nitric oxide* forms the alkali hyponitrite, KNO. C. Hugot found that with *phosphorus* and sodammonium, $PNa_3.PH_3$,

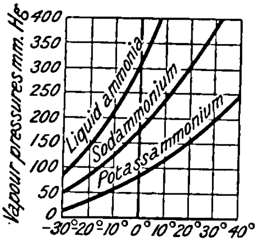

FIG. 45.—Vapour Pressure Curves.

is formed; with *arsenic*, $AsNa_3.AsH_3$; and with *phosphine*, J. A. Joannis obtained $PH_2.Na$. Sodammonium is attacked by *antimony*. H. Moissan obtained with dry *carbon monoxide*, potassium carbonyl, KCO; E. Rengade obtained with *carbon dioxide* at $-50°$, sodium carbonate and hydrogen, and at $-25°$ to $-35°$, some formate is also produced. H. Moissan obtained with *acetylene*, $C_2Na_2.C_2H_2$, or C_2Na_2, according to the conditions—*vide* carbides. Potassammonium yields $C_2K_2.C_2H_2$. J. A. Joannis found that sodammonium forms with *lead*, a lead-sodium ammonia compound: potassammonium attacks *mercury;* and *sodium chloride* forms a complex sodium chloroamide. C. A. Kraus and H. F. Kurtz found that when metallic salt is added to a soln. of a more electropositive metal in ammonia, precipitation of the metal (from the salt), either alone or as a compound with the other, may occur. The theory of the various possible cases is fully discussed. Salts of mercury, cadmium, zinc, tin, lead, antimony, bismuth, and thallium reduced thus by sodium all give compounds with sodium, but silver is precipitated alone. Some of the intermediate compounds of sodium with mercury, tin, and lead are not stable in contact with the soln., but decompose to compounds poorer in sodium. Mercuric ethyl chloride, by the same treatment (with excess of sodium), gives the compound NaHg, identical with that obtained by reducing ordinary mercury salts. In addition, the compounds NaCd, $NaZn_4$, Na_4Sn, Na_4Pb, and Na_3Tl_2 were formed. In the case of calcium, in place of sodium, CaAg, Ca_7Zn, Ca_3Hg_2, Ca_2Pb_3, and Ca_5Sn were thought to be formed.

H. Moissan reported that **lithammonium,** $LiNH_3$, is obtained as a brownish-red solid when the liquid produced by the action of dry ammonia gas on lithium at ordinary temp. is rapidly heated to 70°; if produced at lower temp., it always contains more ammonia than that demanded by the above formula. When allowed to remain for any length of time at the ordinary temp., a soln. of lithium ammonia in liquid ammonia yields lustrous, transparent crystals of lithamide. This reaction proceeds more rapidly at 65°–80°, and appears to be independent of the press. If solid lithammonium heated at 50° or 60° is exposed to the rapid action of the vacuum pump, ammonia is evolved and crystalline lithium is obtained; if the exhaustion is effected more slowly at ordinary temp. hydrogen is also evolved, and the residue consists of lithium and lithamide. Lithammonium is oxidized when exposed to air. With ammonium chloride, hydrogen, ammonia, and lithium chloride are formed. Acetylene forms $C_2Li_2.C_2H_2.2NH_3$. If the blue soln. of lithammonium is allowed to stand 24 hrs. at ordinary temp. there is formed a brownish-red substance which has the composition $Li(NH_3)_3$. H. Moissan obtained with methylamine and lithium, $LiNH_3.NH_2$. C. A. Kraus measured the vap. press. of a sat. soln. of lithium in liquid ammonia, *i.e.* of $LiNH_3$, prepared by H. Moissan, and found 9·98 cms. at 20·3°; 9·53 cms. at 19·3°; 5·70 cms. at 9·75°; and 3·31 cms. at 0°. From the relation $Q=4{\cdot}6T_1T_2/(T_2-T_1)(\log p_2/p_1)$, he obtained 8698 cals., which represents the heat evolved when a mol of ammonia vapour combines with the metal under equilibrium conditions to form a sat. soln. By studying the vap. press. curves, F. Benoit observed that soln. of lithium in liquid ammonia contain $Li.4NH_3$, which easily decomposes into lithamide, hydrogen, and ammonia. There is no evidence of $Li.NH_3$. The mol. wt. corresponds with $Li_2.8NH_3$, and its heat of formation: $2Li_{solid}+8NH_{3gas}=Li_2.8NH_{3liq.}+8{\cdot}67$ Cals. C. A. Kraus and W. C. Johnson were unable to verify this for liquid ammonia at $-39{\cdot}4°$ containing between 3·61 to 60 mols of ammonia per gram-atom of lithium. The curve is continuous, rising rapidly with increasing dilution, and then more slowly until the region of two liquid phases is reached, when the press. remains constant at 540 mm. —that of ammonia alone is 555 mm. There is no evidence of the formation of compounds of the alkali metals with ammonia of the ammonium type.

H. Moissan found that **cæsammonium,** $CsNH_3$, is formed when ammonia under atm. press. acts on cæsium in the form of fine wire at 40°. On cooling by means of a mixture of acetone and solid carbon dioxide, a blue liquid is obtained from which the crystalline, brass-coloured, cæsammonium separates. When brought into contact with the air, it takes fire. It dissolves in liquid ammonia to form a blue, oily soln.; if this soln. be warmed or placed under reduced press., dissociation takes place and small crystals of cæsium are obtained. Rubidium is not attacked by liquid ammonia at —75°, but at a slightly higher temp. action takes place, and a blue soln. containing **rubidammonium**, $RbNH_3$, is formed. Rubidium is first attacked by gaseous ammonia at atm. press. at —3°. The metal-ammonium easily dissociates and leaves small, prismatic crystals of rubidium. The reactions with acetylene resemble those with the other alkali metals.

While T. Weyl, J. A. Joannis, and H. Moissan consider that the soln. of the alkali metals in liquid ammonia contain compounds of ammonia and the metal, C. A. Seely, C. A. Kraus, and O. Ruff and E. Geisel say that the soln. are soln. of the metal in ammonia or mixtures of the metal with a soln. of the metal in liquid ammonia. If the copper-coloured substances be squeezed between folds of cloth in a filter-press, O. Ruff and E. Geiscl separated solid metal, and a sat. soln. of the metal in liquid ammonia. Following C. A. Kraus, let *FE*, Fig. 46, represent the composition of soln. of sodium in ammonia in equilibrium with solid ammonia. Soln. with a conc. between *d* and *e* are in equilibrium with soln. of conc. between *d* and *e* along the curve *EDC* so that two liquid phases are present. Solutions represented by points on the curve *CB* soln. have a concentration between *b* and *c*, and are in equilibrium with solid ammonia, while solutions represented by points on *BA* are in equilibrium with solid sodium, consequently, *AB* is the solubility curve of sodium in ammonia. On cooling, the soln. whose composition lies between *e* and *c*, separates into two liquid phases; the two soln. are mutually soluble in all proportions at the point *D* which has not been located exactly—probably it is not far from —50°. A solution of the metal in ammonia will form a two-component system (NH_3 and metal) with two phases (soln. and vapour) so that if ammonia be gradually withdrawn from the system, the press. will vary with the conc. of the soln. (bivariant system), and become constant only when a third phase appears (univariant system). If the third phase subsequently disappears, the press. will again vary (bivariant system) as ammonia is withdrawn. If the third phase changes abruptly, producing a new (third) phase, the vapour press. will change to a new constant value. The system under consideration does not change in this way when the supposed metal-ammonia compounds separate from the soln., for if ammonia gas be gradually withdrawn from a vessel containing a very dil. soln. of, say, sodium in ammonia, the vapour press. decreases with increasing conc. until the soln. separates into two layers, a dark blue, more dil. soln. below, and a bronze-coloured, more conc. soln. above. The vapour press. remains constant until all the dil. soln. has disappeared. The vapour press. again decreases with increasing conc. until the soln. is sat. and a solid begins to separate, when the press. remains constant until nothing but ammonia and free metal remain. It might therefore be expected that the solid which first separates is also free metal, but J. A. Joannis says that it is not so because the solid which initially separates has the same colour as the soln., and it also has a metallic reflection, while the free metal has a silver-white metallic reflection; J. A. Joannis also assumes that the dissociation press. of the alleged compound is exactly equal to the vapour press. of the sat. soln. in order to explain the passage from compound to metal without an appreciable change of press. However, the fact discovered by J. A. Joannis that at a series of different temp. there is no change of press. from the moment the solid phase begins to separate until nothing but free metal and gaseous ammonia remain, is not in harmony with the phase rule if a compound is initially formed which dissociates subsequently: $NaNH_3 \rightleftharpoons Na + NH_3$, for

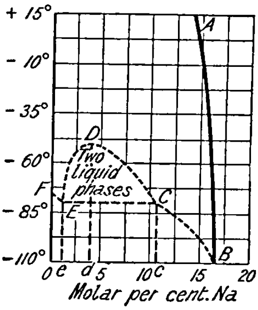

FIG. 46.—Solubility of Sodium in Liquid Ammonia.

the solid phase must consist of nothing more than free metal and a sat. soln. of the metal in ammonia. The system will be invariant—two components and four phases—and such a system can exist only at one definite fixed temp., yet experiment shows that such a system does not exist. Hence, a fourth solid phase cannot be present if the phase rule is valid. There is therefore no satisfactory evidence of the chemical individuality of ammines of the alkali metals.

According to H. Moissan, if ammonia be passed over crystalline calcium, there is a rise of temp.; and if the temp. be kept at 15°–20°, the calcium becomes brownish-red, and swells up, but does not form a soln. as do the alkali metals. Liquid ammonia dissolves a little, forming a blue soln. The product inflames when exposed to air; and at —80°, ammonium chloride gives ammonia and hydrogen. H. Moissan said that the product is *calcium tetrammine*, $Ca(NH_3)_4$. C. A. Kraus, however, showed that this product must have been a mixture because the compound actually formed is **calcium hexammine,** $Ca(NH_3)_6$. He found that if ammonia be gradually withdrawn from a sat. soln. of calcium in ammonia at —33°, the vap. press. gradually falls as represented by the curve *AB*, Fig. 47; at *B*, the soln. separates into two layers, a dil. and a conc. soln., and the vapour press. remains constant, *BC*, until the dil. soln. disappears at *C*. Afterwards, the press. gradually falls from *C* to *D* as ammonia is withdrawn, until, at a press. of 471·8 mm. (—32·5°) a solid compound appears, and this press. remains constant, *DE*, until the sat. soln. disappears, when the press. falls abruptly from *E* to *F*—about 1·8 mm., and the metal calcium appears. This press., *EF*, remains constant so long as the solid compound remains undecomposed. Analysis agreed with the hexammine formula. The solid compound does not lose its ammonia in steps, thus showing that only one compound is formed which dissociates directly into the metal and ammonia: $Ca(NH_3)_6 \rightleftharpoons Ca + 6NH_3$. There is no sign of H. Moissan's $Ca(NH_3)_4$ on the vap. press. curve. W. Biltz and G. F. Hüttig gave 10·32 Cals. for the heat of formation of calcium hexammine. The old names of these compounds and their supposed constitution as compounds of the alkali metals with ammonia are based on the hypothesis that the compounds $NaNH_3$ and KNH_3 have an ammonium structure; but since these substances do not exist, and since the known compounds of the metals of the alkaline earths are formed by the union of the metal with six mols. of ammonia per atom of metal, O. Ruff and co-workers say that the ammonium theory must be abandoned, and with it, the term metal-ammonium. The term, however, is good enough when meaning a soln. of the alkali metal in liquid ammonia. The pasty condition of the calcium-ammonium compound is attributed by E. Botolfsen to the presence of traces of sodium, and he believed that calcium can form a number of ammines with ammonia. When the calcium ammine is heated in vacuo, at about 34°, it decomposes explosively, forming calcium nitride and hydride, and hydrogen gas. According to G. Roederer, when dry liquid ammonia acts on strontium at —60°, reddish-brown crystals of **strontium hexammine,** $Sr(NH_3)_6$, are formed, and they dissolve in liquid ammonia to give a deep blue soln. The dissociation press. of the crystals is about 10 mm. at —40°, and 760 mm. at 46°. When strontium hexammine is exposed under reduced press., it decomposes slowly at 20°, and very rapidly above this temp., evolving a mixture of ammonia and hydrogen and leaving a white mass of strontiamide, $Sr(NH_2)_2$. W. Biltz and G. F. Hüttig gave 9·91 Cals. for the heat of formation of strontium hexammine. G. Roederer added that when a soln. of strontium hexamine is treated with carbon monoxide at —45°, a dull yellow, pulverulent mass of strontium carbonyl, $Sr(CO)_2$, is obtained; this becomes bright yellow on exposure to moist air, forms a limpid, yellow soln. with water, and blackens when

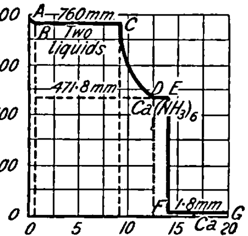

FIG. 47.—The Solubility of Calcium in Liquid Ammonia.

heated under reduced press., yielding a mixture of strontia, strontium carbonate, and carbon. By the action of oxygen on strontium hexammine, dissolved in ammonia soln., cooled to —55°, the deep bluish-black colour lightens and finally disappears, and, on allowing the ammonia to evaporate, a mixture of strontia and strontium dioxide is obtained. Nitrogen dioxide also reacts with strontium hexammine, dissolved in ammonia soln., forming strontium hyponitrite. According to A. Guntz, when barium is treated with gaseous or liquid ammonia, a compound is formed, which R. C. Mentrel showed to be **barium hexammine**, $Ba(NH_3)_6$. The compound is made by passing ammonia over cold barium, when a red solid first appears which, at —23°, passes into a blue liquid, and, at —50°, into a blue oil which is sparingly soluble in liquid ammonia. The compound is stable below —15°, but above this temp., it is converted into an amide. Barium hexammine inflames spontaneously in air, and is violently decomposed by water; it absorbs oxygen, forming a mixture of barium monoxide and dioxide; and with nitric oxide it forms barium hyponitrite. W. Biltz and G. F. Hüttig gave 9·65 Cals. for the heat of formation of barium hexammine. According to A. Guntz and R. C. Mentrel, when barium hexammine, dissolved in liquid ammonia, is treated at —50° with dry oxygen, the latter is absorbed with the formation of a white, gelatinous precipitate of indefinite composition, which, when dissolved in hydrochloric acid, is decomposed with the formation of ammonia and hydrogen dioxide. Carbon monoxide, under the same conditions, produces barium carbonyl, $Ba(CO)_2$, a yellow powder, which is unstable in air, becomes brown at 100°, and incandescent at 250°, forming barium oxide and carbonate and carbon.

According to C. A. Seely, magnesium is insoluble in liquid ammonia, but C. A. Kraus reported that it dissolves in liquid ammonia if precautions be taken to have a clean metal surface in contact with the solvent; and A. G. Loomis obtained an amalgam of **magnesium hexammine**, $Mg(NH_3)_6.Hg_n$, in his study of the system: mercury-magnesium and liquid ammonia. C. A. Seely also said that aluminium, thallium, indium, mercury, and copper are not dissolved by liquid ammonia—*vide supra*, solvent action of liquid ammonia. T. Weyl showed that although liquid ammonia does not act on zinc, yet, when sodammonium is treated with zinc diamminoxide, a *zinc ammine* is formed: $2NaNH_3+ZnO.2NH_3=(NH_3Na)_2O+Zn(NH_3)_2$. The deep blue liquid has a metallic lustre, and decomposes in the course of a day at a temp. of 12°–16°. T. Weyl also prepared a *mercury ammine* by the action of sodammonium on mercuric chloride.

Ammonia gas was found by F. Jones [2] to be absorbed by dry sulphur, and if heat be applied, ammonium sulphide and nitrogen are formed. J. B. Senderens said that these products are formed by the action of aq. ammonia on pure sulphur at ordinary temp., but, according to C. Brunner, sulphur is insoluble in aq. ammonia. If the two be heated for some days in a sealed tube, F. A. Flückiger found that ammonium polysulphide and thiosulphate are formed; and W. P. Bloxam found that heating under press. is necessary for the reaction. According to H. Moissan, liquid ammonia acts at —38° on γ-sulphur; at 15·5°, on β-sulphur; and at —11·5°, on α-sulphur. In a sealed tube, at 20°, liquid ammonia dissolves about 30 per cent. of sulphur, forming a purple-red soln. of what he called **sulphammonium,** $S(NH_3)n$, he regarded this as a definite compound—between 0° and 20°, the composition corresponded with $S(NH_3)_4$, or $(NH_3)_2S.2NH_3$; at —23°, the formula corresponded with $(NH_3)_3S$, or $(NH_3)_2S.NH_3$, so that no definite formula can be given for the alleged compound. G. Gore, C. A. Seely, E. C. Franklin and C. A. Kraus, and C. Hugot considered the reddish-purple liquid to be a simple soln. of sulphur in liquid ammonia. H. Moissan obtained sulphammonium as a purple-red soln. by the action of liquid ammonia on sulphur in a sealed tube. If the soln. be cooled 4°–5° below the f.p. of liquid ammonia, it becomes solid without the separation of sulphur. If the dil. soln. be heated to 90°, the intensity of the colour diminishes, and at 131°, the critical temp. of ammonia, the liquid becomes colourless, and crystals of sulphur separate out. The liquid when cooled to 100°

again becomes colourless, and the original purple-red colour is restored at ordinary temp. If sulphammonium be a simple soln., said H. Moissan, it is not clear how at 100° the solid and solvent can exist beside one another. O. Ruff and E. Geisel thought that the soln. might contain hydrogen sulphide, nitrogen sulphide, and *thiodiimide*, $(NH)_2S$, or *dithiodiimide*, $(NH)_2S_2$. They represent the first stage in the formation of sulphammonium as a reversible reaction: $10S+4NH_3 \rightleftharpoons 6H_2S+N_4S_4$, the two products on the right may form compounds with ammonia. The hydrogen sulphide can be precipitated with silver iodide, and nitrogen sulphide obtained from the residue. The same final state can be obtained by the action of hydrogen sulphide on a soln. of nitrogen sulphide in liquid ammonia. The blue sulphamide soln. can also be obtained by the action of liquid ammonia and hydrogen sulphide on lead dithiodiimide, $PbN_2S_2+3H_2S=PbS+2NH_3+4S$; and on mercury thiodiimide, $HgN_2S+3H_2S=HgS+2NH_3+3S$. The soln. is decolorized by the addition of ammonium sulphide which presumably forms a polysulphide, while a small proportion of ammonium sulphide added to a liquid ammonia soln. of nitrogen sulphide produces a blue soln. O. Ruff and E. Geisel say that all these facts, and possibly also the dichroism of the sulphammonium soln.—red in transmitted, blue in reflected light—are in harmony with the assumption that the intense purple-coloured substance is partly a colloidal sol. of elemental sulphur in liquid ammonia, and partly a mixture of the products of a reaction between sulphur and ammonia. This hypothesis is not contradicted by any of H. Moissan's observations. P. Lebeau and P. Damoiseau claim that if the materials be all thoroughly dried, the reactions described by O. Ruff and E. Geisel do not occur. F. W. Bergstrom showed that the action of soln. of sulphur in liquid ammonia on the metal cyanides indicates that the equilibrium: $10S+4NH_3 \rightleftharpoons 6H_2S+N_4S_4$ probably does occur, but there are quite a number of other reactions involved: *e.g.* $10S+4NH_3 \rightleftharpoons S_4N_4+6H_2S$; $H_2S+2NH_3=(NH_4)_2S$; $S_4N_4+2NH_3=2S(NH)_2+S_2(NH)_2$; $(NH_4)_2S+nS=(NH_4)_2S_{n+1}$; $(NH_4)_2S_{n+1} \rightleftharpoons (NH_4)_2S_n+S$; etc.

According to O. Ruff and L. Hecht, the f.p. curve, Fig. 48, of mixtures of sulphur and ammonia falls from −77·34° to a eutectic at about −79·7° and 16·3 per cent. of sulphur; it then rises to a maximum at −78·3° and 24 per cent. of sulphur corresponding with **sulphur hexammine,** $S(NH_3)_6$; the curve then falls to −84·6° at a composition corresponding with **sulphur triammine,** $S(NH_3)_3$. The existence of this compound is shown by the break in the solubility curve, Fig. 48. Both compounds are probably associated to form doubled molecules in soln. H. Moissan's *sulphur diamine*, $S(NH_3)_2$, is not present in the system. It was therefore inferred that the assumed equilibrium $10S+4NH_3 \rightleftharpoons 6H_2S+N_4S_4$ is of minor importance as most of the sulphur is present in the form of ammines. O. Ruff and L. Hecht also examined the absorption of light by the soln., and the results indicate the probable existence of several compounds in the soln. A. K. Macbeth and H. Graham obtained **sulphur hexitamide,** or **hexasulphamide,** $S_6(NH_2)$, by adding alcohol to mixed chloroform soln. of ammonia and sulphur monochloride to precipitate the nitrogen tetrasulphide, and evaporating the mother-liquor. The colourless, square plates melt at 105°; they are insoluble in water, but soluble in organic solvents. This compound gives a coloration with alcoholic soln. of potassium hydroxide, or of organic bases. The coloration may be due to a salt of a nitrogen-sulphur acid.

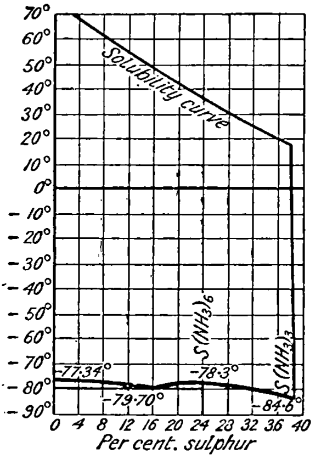

FIG. 48.—Equilibrium Diagram of the System: Sulphur-Ammonia.

H. Moissan found that when a mixture of nitrogen, ammonia, and sulphur is exposed to 45 atm. press. at —12°, or 20 atm. at —40°, ruby-red crystals of sulphammonium are formed. These dissolve in an excess of liquid ammonia. The red colour can be detected when but 0·00061 per cent. of sulphur is present; a trace of water imparts a greenish colour to the soln. The liquid freezes at —85° to a red mass without the separation of sulphur. If the soln. is not sat., white plates of solid ammonia melting at —75° can be detected when the solid is melting. The vap. press. curve of sulphammonium is nearly parallel to that of liquid ammonia. The liquid shows a characteristic absorption spectrum—with dil. soln., there is an absorption band cutting off the yellow and orange parts of the spectrum, and another cutting off the blue with portions of the green and violet; with conc. soln., all except a green band and the least refrangible portion of the red end of the spectrum is cut off. Sulphammonium is soluble in absolute alcohol, dried ether, and many other solvents. These soln. are stable at low temp. If ether cooled to —80° be added to a soln. of sulphammonium, a homogeneous purple-red liquid is formed, but if more ether is added, the soln. becomes blue; at —40°, the blue soln. is decolorized with the separation of sulphur. The soln. prepared with chloroform at —80° is purple-red, but at 15°, it suddenly becomes yellow with the separation of crystalline sulphur. Some liquids which do not mix with the sulphammonium may react with it—benzene, for instance, gives a brown soln., carbon disulphide, a blue one; carbon tetrachloride, colourless crystals and an orange-yellow compound which dissociates at ordinary temp.

According to O. Ruff and E. Geisel, if sulphammonium be slowly evaporated in air, a pale red mixture of sulphur with a number of other substances is formed. After standing for a long time, the mixture gradually loses its colour, and sulphur alone remains. If a quick current of hydrogen be passed through the evaporating liquid, the liquid ammonia first volatilizes, then follows ammonium sulphide, and nitrogen sulphides remain. The gases which pass off contain some hydrogen sulphide. H. Moissan said the sulphammonium can transform many substances into sulphides. Brown ammoniacal soln. of iodine are decolorized by an excess of sulphammonium with the evolution of ammonia. Molten selenium has no action; a soln. of calcium in ammonia forms white calcium sulphide; if the sulphammonium be in excess, red crystals are formed. At ordinary temp., sulphammonium reacts with mercury, forming crystals which dissociate and produce mercury sulphide; dried calcium oxide forms red crystals and a solid which easily dissociates; zinc oxide forms orange-yellow crystals; sodium chloride and bromide are not attacked; anhydrous magnesium chloride forms a yellow crystalline compound; lead chloride forms yellow crystals which dissociate in air under atm. press.; mercuric chloride produces a dark-coloured substance insoluble in liquid ammonia, but which dissociates in air to mercuric sulphide.

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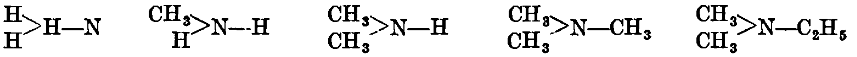
§ 21. The Substituted Ammonias—The Amines, Amides, and Imides

> The eye may rest with complacency upon the simple beauty of the law which governs the construction of bodies belonging to the type of ammonia.—A. W. HOFMANN.

The hydrogen atoms of ammonia can be replaced, one by one, by equivalent radicles—methyl, CH_3 ; ethyl, C_2H_5 ; . . . to form a series of compounds called the **amines** or **substituted ammonias** in which nitrogen is undoubtedly tervalent. The amines are distinguished as primary, secondary, or tertiary, according as one, two, or three of the hydrogen atoms in ammonia are replaced by these radicles. Thus:



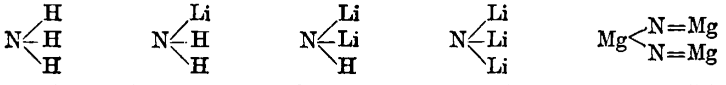
$$\genfrac{}{}{0pt}{}{H}{H}{>}H{-}N \qquad \genfrac{}{}{0pt}{}{CH_3}{H}{>}N{-}H \qquad \genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}N{-}H \qquad \genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}N{-}CH_3 \qquad \genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}N{-}C_2H_5$$

Ammonia. Methylamine. Primary. Dimethylamine. Secondary. Trimethylamine. Tertiary. Dimethylethylamine. Tertiary.

The existence of the alkylamines was predicted by J. von Liebig,[1] 1837 ; in 1849, A. Wurtz obtained the primary alkylamines; and in 1851, A. W. Hofmann prepared the primary, secondary, and tertiary alkylamines, and also the alkylammonium bases or the quarternary ammonium bases in which all four atoms of the ammonium group are replaced by the alkyl radicles. The basic character of ammonia is retained by the amines, and since the alkyl radicles are themselves basic, the aliphatic amines are even more basic than ammonia itself. W. Ostwald made an estimate of the basicity of the ethyl ammonias, and found the relative strengths of these bases:

NH_3	$(C_2H_5)NH_2$	$(C_2H_5)_2NH$	$(C_2H_5)_3N$	$(C_2H_5)_4NOH$
4·8	20·5	28·3	20·2	128·0

The basic properties of the aromatic amines decrease with the number of radicles introduced ; the primary aromatic amines are stable ; the secondary aromatic amines are decomposed by water ; and the tertiary aromatic amines are unstable. In organic chemistry, compounds containing the monadic group NH_2 are called **amines** or **amides** ; and compounds with the dyadic group NH are called **imides**. The existence of compounds like



$$N\begin{cases}H\\H\\H\end{cases} \qquad N\begin{cases}Li\\H\\H\end{cases} \qquad N\begin{cases}Li\\Li\\H\end{cases} \qquad N\begin{cases}Li\\Li\\Li\end{cases} \qquad Mg{<}\genfrac{}{}{0pt}{}{N{=}Mg}{N{=}Mg}$$

Ammonia. Lithium amide. Lithium imide. Lithium nitride. Magnesium nitride.

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[2] F. Jones, *Journ. Chem. Soc.*, **29**. 641, 1876 ; W. P. Bloxam, *ib.*, **67**. 277, 1895 ; C. Brunner, *Dingler's Journ.*, **151**. 371, 1859 ; *Mitt. Bern*, 76, 1858 ; F. A. Flückiger, *Zeit. anal. Chem.*, **2**. 398, 1863 ; *Pharm. Vierteljahr.*, **12**. 321, 1863 ; J. B. Senderens, *Compt. Rend.*, **104**. 58, 1887 ; H. Moissan, *ib.*, **126**. 685, 1898 ; **132**. 510, 1901 ; P. Lebeau and P. Damoiseau, *ib.*, **144**. 1422, 1907 ; O. Ruff and E. Geisel, *Ber.*, **38**. 2659, 1905 ; O. Ruff and L. Hecht, *Zeit. anorg. Chem.*, **70**. 49, 1911 ; A. K. Macbeth and H. Graham, *Proc. Irish Acad.*, **36**. 31, 1923 ; C. Hugot, *Ann. Chim. Phys.*, (7), **21**. 5, 1900 ; C. A. Seely, *Journ. Franklin Inst.*, **91**. 110, 1871 ; *Chem. News*, **22**. 217, 1898 ; E. C. Franklin and C. A. Kraus, *Amer. Chem. Journ.*, **20**. 821, 1898 ; G. Gore, *Proc. Roy. Soc.*, **21**. 140, 1873 ; F. M. Bergstrom, *Journ. Amer. Chem. Soc.*, **48**. 2319, 1926.

in which one or more hydrogen atoms is replaced by a metal, is sometimes cited as evidence that ammonia is a weak tribasic acid.

In 1809, H. Davy,[2] and J. L. Gay Lussac and L. J. Thénard independently sought to determine the composition of ammonia by passing the gas over sodium heated in a glass retort to about 300°. The glass of the retort was considerably corroded, and in the case of sodium, an olive-green crystalline mass was obtained. H. Davy's investigation of the action of water, J. L. Gay Lussac and L. J. Thénard's study of the action of heat, and F. Beilstein and A. Geuther's work on the action of hydrochloric acid on the olive-green compound showed that it is an amide of the alkali metal—**sodium amide** or **sodamide,** NH_2Na. When made in glass vessels, the sodamide is contaminated with products derived from its reaction with glass. It is best made in a silver, iron, or nickel vessel, when the resulting product is white. A. W. Titherley used an iron vessel in which the sodium was heated to 300°–400° in a current of dry ammonia. A. Guntz and F. Benoit used a similar process. L. M. Dennis and A. W. Browne prepared it in the apparatus depicted in Fig. 49.

A sheet iron vessel, *A*, with riveted joints and a double bottom, has a grooved rim *B* into which fits a cover *C*. The cover has three tubular openings fitted with rubber stoppers—one *D* is an inlet for ammonia, another *E* is the outlet, and the third is for a thermometer *F*. The ammonia inlet-tube leads into a nickel dish *G* which contains clean dry sodium, and stands upon a little tripod to prevent direct contact with the hot bottom of the iron vessel *A*. When the lid *C* is in position, the annular space of the rim is packed with sand. The vessel *A* rests on a thick iron plate heated by a suitable burner. The ammonia is dried in a tower of soda-lime; and the sodium heated to 100° or 400°. Hydrogen mixed with the excess of ammonia escapes. The reaction is represented $2NH_3+2Na=2NH_2Na+H_2$.

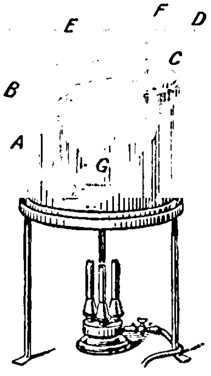


Fig. 49.—The Preparation of Sodamide.

L. Wöhler and F. Stang-Lund devised a special apparatus for the preparation of sodamide of a high degree of purity. F. Rössler passed the ammonia into fused sodium; once the reaction has started external heating is unnecessary. A. W. Titherley also made the amide by heating sodium oxide in a current of ammonia; J. A. Joannis, by keeping sodammonium for some time at ordinary temp.; and H. Moissan, by the action of ammonia on sodium hydride in the cold. T. Ewan made alkali amides by bringing a liquid ammonia soln. of the alkali metal and one of its salts—*e.g.* the cyanide—in contact with high carbon iron or steel as a catalyst; or by electrolyzing a soln. of an alkali salt—*e.g.* the cyanide—in anhydrous ammonia in the presence of high carbon steel or iron as catalyst, and with an alkali metal amalgam as cathode. The corresponding **potassium amide,** or **potassamide,** KNH_2, was made by H. Davy, and J. L. Gay Lussac and L. J. Thénard in a similar way to that they employed for sodamide. F. M. Baumert and H. H. Landolt, and A. W. Titherley made the amide in an analogous manner. The Badische Anilin- und Soda-fabrik made the alkali amides by passing ammonia gas into soln. of the alkali metals in fused anhydrous alkali hydroxide. The action takes place at about 275°. H. Moissan made **rubidium amide,** $RbNH_2$, by the action of ammonia on rubidium hydride, and by allowing rubidammonium to stand for some time. A. W. Titherley made it by the action of ammonia on rubidium at 200°–300°. H. Moissan also made **cæsium amide,** $CsNH_2$, in a similar way, and also found that a mixture of amide and nitride is formed when nitrogen is passed over heated cæsium hydride. E. Rengade made it by the action of dry ammonia on cæsium at 120°; and by the spontaneous decomposition of a soln. of cæsium in liquid ammonia. Clean lithium when exposed to ammonia in the cold acquires a bluish-white crust, but suffers no further change. A. W. Titherley made **lithium amide,** $LiNH_2$, by the action of ammonia on lithium at 400°, and H. Moissan, by heating a soln. of lithium in liquid ammonia to 65°–80°; and O. Ruff and H. Goerges also obtained it by the interaction of lithium and liquid ammonia in a sealed tube at ordinary temp. for two weeks. F. W. Dafert and R. Miklauz observed that in the action of nitrogen on lithium hydride, of hydrogen on lithium nitride, or of mixtures of nitrogen and hydrogen or ammonia on lithium hydride or nitride, lithium imide, lithium amide, or trilithium amide, or mixtures of these three substances are formed, the final product depending on the temp. and other experimental conditions. The amide can be readily obtained by the action of ammonia on amorphous lithium nitride at temp. between 130° and 350°, or on crystalline lithium nitride from 410° to 430°, or on lithium hydride from 440° to 460°, the changes taking place according to $Li_3N+2NH_3=3LiNH_2$ and $LiH+NH_3=LiNH_2+H_2$.

Lithium amide was stated by A. W. Titherley to furnish long, colourless, transparent needles or a white crystalline mass, which, when melted, appears pale green. O. Ruff and H. Georges described it as forming white, lustrous crystals, consisting of regular hexahedra mixed with octahedra and tetrakishexahedra, and of sp.gr. 1·178 at 18·5°. F. Beilstein and A. Geuther said that sodium amide furnishes crystalline masses which appear brown when cooling but olive-green or flesh-red when cold. The colour, said A. W. Titherley, is due to the presence of impurities, for sodamide can be readily obtained in white crystalline masses with a conchoidal fracture. J. L. Gay Lussac and L. J. Thénard's preparation of potassium amide was greenish-brown; F. M. Baumert and H. H. Landolt's was yellowish-brown or flesh-red, and in thin layers white; and A. W. Titherley's, a white mass with a waxy appearance. Rubidium amide was obtained by A. W. Titherley as a white, crystalline mass; and cæsium amide, by E. Rengade, in microscopic prisms or plates. O. Ruff and H. Georges said that lithium amide has a m.p. of 573°–575°, and it may be sublimed in ammonia. According to A. W. Titherley, lithium amide melts at 380°–400°; sodium amide softens at 149°, melts at 155°, and sublimes at 400°; potassium amide melts at 270°–272°; rubidium amide, at 285°–287°; according to C. A. Kraus and E. J. Cuy, sodium amide melts at 206·4°; and potassium amide, at 329·0°; J. M. McGee gave 208° for the m.p. of sodamide; and L. Wöhler and F. Stang-Lund, 210° for sodamide, and 338° for potassamide. No other breaks occurred in the cooling curves. According to E. Rengade, cæsium amide melts at about 260°. R. C. Mentrel said that when lithium amide is heated to 430° in a stream of ammonia, it begins to decompose giving off hydrogen and nitrogen and acquiring a yellow colour, but the amide is re-formed if the product is cooled in ammonia gas. In vacuo, decomposition begins at 370°; after heating to 450°, there remains white lithium imide, Li_2NH, or a mixture of imide and nitride. Decomposition is completed at 750°–800°. C. A. Kraus and E. J. Cuy's results for the m.p. of mixtures of sodium and potassium amides are summarized in Fig. 50. There is a eutectic at 92° with 33 molar per cent. of potassium amide, and a break in the curve at about 120° corresponding with the existence of an unstable sodium potassium triamide, $NaNH_2.2KNH_2$, which is largely dissociated in the molten mixture. When sodium amide is melted, it furnishes a pale green liquid which becomes dark green at 500°, and then appears to boil owing to its decomposition. In vacuo, decomposition begins at 330°, and is complete at 440°. The product obtained at 390° is a mixture of sodium, sodium nitride, and sodium amide. J. L. Gay Lussac and L. J. Thénard said that decomposition proceeds $3NaNH_2=Na_3N+2NH_3$, but A. W. Titherley found that sodamide begins to decompose into its elements at 500°–600°; and concluded that J. L. Gay Lussac and L. J. Thénard's nitride was a mixture derived from impurities in the sodium, and from the action of sodium on the glass during their preparation of the amide. J. L. Gay Lussac and L. J. Thénard found that potassium amide decomposes when heated; and A. W. Titherley noted that the colour of the

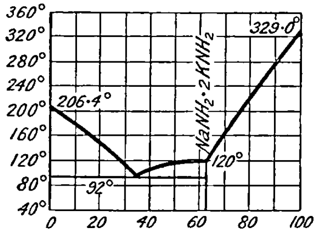


FIG. 50.—The Freezing Points of Mixtures of Potassium and Sodium Amides.

molten amide darkens with rise of temp. being almost black at 500°. A. W. Titherley said that the amide decomposes only when heated in glass vessels; in silver vessels the amide begins to sublime at 400°, and it distils rapidly in a current of hydrogen at 400°–500°. The product of the decomposition is not K_3N, but the amide is resolved into its elements. Rubidium amide melts to a greenish-brown viscid liquid, and becomes darker in colour as the temp. rises. The brown liquid distils at 400°. R. de Forcrand gave for the heat of formation $NH_{3gas}+Na_{solid}=H_{gas}+NaNH_{2solid}+20·84$ Cals.; with liquid ammonia, 16 Cals.; and $NaNH_{3solid}=H_{gas}+NaNH_2+15·64$ Cals. The heat of soln. at 20°–22° is 31·04 Cals. A. Guntz and F. Benoit gave 86·70 Cals. for the heat of formation of lithium amide, $LiNH_2$. H. Davy said the alkali amide is a non-conductor of electricity. J. M. McGee said that while sodamide melts at 208°, it has a sp. conductivity of 1·665 mhos at 210°—above this temp. the platinum electrodes act catalytically in the decomposition of sodamide into ammonia and sodium imide or nitride. According to L. Wöhler and F. Stang-Lund, molten sodamide or potassamide conducts a current electrolytically, due to the ionization $NaNH_2=Na^{\cdot}+NH'_2$. Hydrazine is not formed at the anode, but rather ammonia and nitrogen, the discharge of the anion taking place according to the equation $6NH'_2+6\oplus=4NH_3+N_2$. The formation of hydrazine was probably prevented by the catalytic action of the sodamide. The sp. conductivity at 210° is 0·593 mho for sodamide; and at 340°, 0·389 mho for potassamide. The decomposition voltage at the m.p. is 0·71 volt for sodamide and 0·87 volt for potassamide, the former having a temp. coeff. of $1·52\times10^{-3}$ volt. E. C. Franklin and C. A. Kraus studied the electrical conductivity of sodium amide in liquid ammonia.

When kept in dry stoppered bottles, sodamide gradually changes in colour from white to yellowish-brown owing to the formation of oxidation products—hyponitrites, nitrites, etc.—since no change occurs if the amide be well protected from air. According to E. Drechsel, if exposed to air, the amide acquires a crust of nitrite. Sodium amide is hygroscopic and readily decomposes when exposed to moist air. F. W. Bergstrom said that the elements react with soln. of amides in liquid ammonia provided that the salts of the element are soluble in ammonia: $M+nA(NH_2)\rightleftharpoons nA+M(NH_2)_n$, where M represents a metal of valency n, and A the alkali metal. This agrees with E. C. Franklin's statement that potassium amide in liquid ammonia is a base like potassium hydroxide is in water. A. W. Titherley found that sodium amide does not react to any appreciable extent when heated with **hydrogen** in a closed vessel; but F. D. Miles showed that sodium hydride is formed when the amide is heated between 200° and 300° in a stream of hydrogen: $NaNH_2+H_2=NH_3+NaH$. A. Guntz and F. Benoit studied the reaction. J. L. Gay Lussac and L. J. Thénard, and H. Davy found that when potassium amide is heated in **oxygen,** or **air,** there is a vigorous combustion and nitrogen is set free and potassium hydroxide is formed. E. Rengade said that when oxygen is passed into a soln. of potassium amide in liquid ammonia the main reaction is: $2KNH_2+3O=KNO_2+KOH+NH_3$—a little nitrate is produced. Cæsium amide acts similarly. H. Schrader found that when the alkali amides are exposed to air, they undergo autoxidation with formation of nitrite, hydroxide, and ammonia. When finely-divided sodamide is exposed to air in presence of a little water, a yellowish-red product is formed, which has now been shown to be **sodium amidoperoxide,** probably of the formula $NaNH_2O_2$. After 58 days, a sample was found to contain 0·44 molar per cent. of peroxide and 6·9 mols. per cent. of nitrite calculated on the sodamide taken. In dry air autoxidation does not take place at the ordinary temp., but at 100°–110° C. it proceeds slowly, 9·5 mols. per cent. of peroxide being formed in the course of 170 hrs. The peroxide is stable in dry air, but in moist air is changed into a white substance, the aq. soln. of which gives the peroxide reaction. J. L. Gay Lussac and L. J. Thénard, and H. Davy showed that potassium amide reacts vigorously with **water,** forming potassium hydroxide; the reaction may be accompanied by inflammation. If an excess of water be avoided, ammonia eq. to the nitrogen present is evolved; no hydrogen is formed unless the free metal be present. L. Wöhler and F. Stang-Lund said that the reaction with water is more regular if the amide be previously moistened with alcohol. E. Rengade said that the reaction with cæsium amide and water in air proceeds with incandescence; and without air, $CsNH_2+H_2O=CsOH+NH_3$. According to W. P. Winter, when sodium amide is treated with water, it behaves not unlike sodium, since it forms a globule which floats about on the water and at last explodes—sodium hydroxide and ammonia soluble in water are produced: $NaNH_2+H_2O \rightarrow NaOH+NH_3$; while hydrogen and a little free nitrogen are formed as secondary products of the reaction. The proportion of nitrogen to hydrogen is lower if the sodamide has been made at a relatively low temp., and the proportion increases when the sodamide has been kept for some time so that hydrogen is completely eliminated by preparing the compound at a high temp. or by keeping it a long time in closed bottles.

When heated with the **halogens**, sodamide does not decompose $2NaNH_2+Br_2 \rightarrow 2NaBr+NH_2.NH_2$, but rather decomposes $4NaNH_2+3Br_2 \rightarrow 4NaBr+N_2+2NH_4Br$—*vide infra*, preparation of hydrazine. L. Wöhler and F. Stang-Lund observed that chlorine and iodine do not form hydrazine with the amides, but halogen-substituted ammonias. F. Ephraim said that a soln. of bromine or iodine in benzene develops nitrogen and forms sodium and ammonium halide, but no hydrazine. O. Ruff said that when a soln. of the amide in liquid ammonia is treated with iodine, Na_2NI_3 is formed. F. W. Bergstrom represented the reaction with iodine at $-33°$, $6I+6NaNH_2=6NaI+4NH_3+N_2$. Dil. **hydrochloric acid** furnishes sodium and ammonium chlorides. F. Ephraim found that sodium amide reacts energetically with molten **sulphur**, and a soln. of sulphur in benzene or xylene forms nitrogen, ammonia, and sodium polysulphides. F. W. Bergstrom found that sulphur readily reacts with the amides; while with selenium at $-33°$ or at ordinary temp., there is first formed a white precipitate containing an explosive substance; an excess of **selenium** then yields highly coloured soln. containing polyselenides and a soluble, non-explosive potassium salt of an ammino-acid of this element. At $-33°$, **tellurium** reacts slowly with potassium and sodium amides, but rapidly at ordinary temp. H. Schumann observed a lively reaction between **sulphur dioxide** and potassium amide at 200°, forming $(NH_3)_2SO_2$ and $(NH_3)SO_2$, which sublime, and a mixture containing potassium, sulphur dioxide, and ammonia remains.

H. Krüger and E. Drechsel observed that sodium cyanide is formed when a mixture of sodium amide and **carbon** is heated. F. Beilstein and A. Geuther showed that with **carbon monoxide,** sodamide forms sodium cyanide, $NaNH_2+CO=NaCN+H_2O$; with **carbon dioxide,** it is supposed that sodium carbamate, $CO(NH_2)ONa$, is first formed: $CO_2+NaNH_2 \rightarrow H_2N.CO.ONa$; and this when heated forms sodium cyanate, NaOCN, thus: $NH_2.CO.ONa \rightarrow H_2O+NaOCN$, and disodium cyanamide, $CN.N:Na_2$ is then formed: $NaOCN+NaNH_2 \rightarrow H_2O+CN.N:Na_2$; the complete reaction is represented: $2NaNH_2+CO_2 \rightarrow 2H_2O+CN.N:Na_2$. The reaction is complicated by the presence of moisture. W. P. Winter found that warm water containing carbon dioxide in soln. forms some cyanamide in contact with sodium amide. With **carbon disulphide,** sodamide forms sodium thiocyanate: $NaNH_2+CS_2 \rightarrow H_2S+NaCNS$; and with **carbonyl chloride,** not urea, but a mixture of sodium carbonate and chloride is formed. F. Rössler observed that sodium amide at 120° reacts vigorously with **benzene, alcohol, acetylene,** etc., forming sodium cyanamide, useful as a manure or for the manufacture of sodium cyanide. When heated with **alkyl iodides,** a very small proportion of the corresponding alkylamine is formed, *e.g.* with ethyl iodide, $C_2H_5I+NH_2Na \rightarrow NaI+C_2H_5NH_2$; the main reaction results in the formation of carbon, iodine, etc. Sodamide in the presence of substances capable of reacting with it breaks down in two ways: (i) The rupture of the mol. may occur between the sodium and the amido- or NH_2-group as is the case when it reacts with water;

and (ii) The hydrogen atoms of the amido-group may be replaced one at a time by other radicles, as is the case when sodamide is treated with a boiling soln. of **aniline,** $C_6H_5.NH_2$, in benzene, sodium aniline—*i.e. sodium phenylamide,* $C_6H_5.NH.Na$, is formed; and when a mixture of diphenylamide, $(C_6H_5)_2NH$, and sodamide is heated to about 55°, a rapid action occurs, and sodium diphenylamide is formed: $(C_6H_5)_2N.Na$. A. W. Titherley found that when sodium amide mixed with **silica** is heated to 300°–400°, silicon nitride is formed; **glass** is attacked; and with **boric oxide,** boron nitride is formed; $2NaNH_2+B_2O_3=2BN+2NaOH+H_2O$; **lead borate** is reduced to lead. J. M. McGee said that the solvent action on glass observed by A. W. Titherley was really due to the presence of sodium hydroxide, since no tendency to attack glass was observed below 240°, but at 270°–300°, there is a slight action in 2 or 3 days.

W. Wislicenus showed that with **nitrous oxide** at 150°–250°, sodium azide is formed. A. W. Titherley found that when sodium amide is warmed with **nitrosyl chloride,** nitrogen is evolved: $NOCl+NaNH_2 \rightarrow NaCl+N_2+H_2O$. E. Rengade said that sodium amide is insoluble in liquid **ammonia;** but potassium amide dissolves; and cæsium amide is sparingly soluble. A. W. Browne and F. Wilcoxon found that **sodium nitrate** is ammonolyzed by fused sodamide: $NaNO_3+3NaNH_2=NaN_3+3NaOH+NH_3$; and E. C. Franklin, by warming a mixture of sodium nitrate and amide in liquid ammonia in a sealed tube. W. P. Winter found that yellow **phosphorus** reacts with sodium amide, forming sodium phosphide and other products; F. W. Bergstrom found that red and yellow phosphorus react with potassamide. W. P. Winter observed that the amide also reacts vigorously with **phosphorus pentachloride,** forming a complex series of products of unknown composition. F. W. Bergstrom found that **arsenic** and **antimony** react at ordinary temp. with potassium amide, while the reaction with **bismuth** is very slow. F. Ephraim observed that **arsenic trioxide** is reduced partly to the metal, and sodium arsenite is formed; **antimony trioxide** behaves in an analogous manner.

A. W. Titherley reported that a soln. of **sodium** in sodamide is blue, but J. M. McGee could not make it. According to F. Ephraim, when sodium amide and **magnesium** are heated together, magnesium nitride and sodium are formed. Sodium amide does not react with **iron, tin, copper,** and **silver.** According to F. W. Bergstrom, ammonia soln. of potassium or sodium amide form red soln. with tin: $10Sn+6MNH_2=M_4Sn_8+2SnNM(NH_3)_2$. In the more conc. soln. of potassamide, the formation over the metal of a passive coating, removable by ammonium chloride, prevents reaction. The curves of solubility of tin in the amides plotted against conc. indicate the formation of the compounds Na_4Sn_8 or K_4Sn_8, respectively. **Lead** behaved towards potassamide in an erratic manner; either a green soln. containing polyplumbide and, presumably, ammonioplumbite was slowly formed or there was no action, as was the case with sodamide. A soln. of potassamide (0·6*N*) did not attack **gold,** copper, or **germanium,** and **mercury** was attacked with extreme slowness. Amalgams of lead, bismuth, or silver were unaffected; those of copper and gold were attacked very slowly, and that of tin more rapidly. F. Ephraim found that when sodium amide is heated with **ammonium chloride or iodide,** sodium chloride or iodide is produced. It reacts generally as a reducing agent, thus, the **chlorides of lead, mercury, silver, tin, zinc, and barium** are reduced to the metals; **calcium and potassium chlorides** are not reduced. A. W. Titherley observed no reaction between the amide and **sodium or potassium oxide.** The **oxides of lead, copper, and cadmium** are reduced to metals; **zinc oxide** probably forms zinc nitride; **mercuric oxide** forms sodium amalgam; **chromic anhydride** reacts vigorously when rubbed in a mortar with sodium amide; **chromic oxide** when heated with the amide forms a black substance; **ferric oxide** furnishes iron; **manganese oxide** is not reduced to metal; **tungstic oxide** reacts with incandescence; **vanadium pentoxide** reacts vigorously when heated with sodium amide, and sodium vanadate is formed. Many of the **nitrates** deflagrate when triturated with sodamide, and a mixture of sodamide with **potassium chlorate** explodes. Sodium amide does not easily reduce **sodium chromate.** The **sulphides** of the heavy metals mixed with powdered sodium amide and heated are reduced to the metals; **antimony and arsenic trisulphides** give sulphosalts. The **sulphates** are reduced to sulphides and then to the metals; the **phosphates** are not reduced to phosphides, but to the metal. The alkaline earth phosphates are not reduced. A. W. Titherley found that lithium and rubidium amides react very like sodium amide. J. A. Joannis prepared a complex salt, sodium chloroamide, $NaNH_2.NaCl$, by the action of liquid ammonia on a mixture of sodium and sodium chloride. F. W. Bergstrom studied the action of potassamide in liquid ammonia soln. on **manganese, cobalt and iron salts.**

According to F. W. Dafert and R. Miklauz, when lithium nitride is heated at 220°–250° in a current of hydrogen, **lithium tritammonium,** Li_3NH_4, is formed as a hygroscopic substance which evolves hydrogen and ammonia when treated with water. O. Ruff and H. Georges said that it is a mixture of a mol of lithium amide and 2 mols of lithium hydride being formed in accord with $Li_3N+2H_2=LiNH_2+2LiH$. The resulting mixture of amide and hydride at 340°–480° gives lithiumimide and ammonia, from the decomposition of the amide, and the ammonia immediately combines with the hydride, forming imide and hydrogen, so that the total reaction is given by the equation: $2LiNH_2+4LiH=2Li_2NH+2LiH+2H_2$. This is supported by the fact that lithium amide does decompose into the imide and ammonia at 240°–450°, and that at a slightly higher temperature lithium hydride reacts with ammonia with the formation of lithium amide. F. W. Dafert and R. Miklauz based their hypothesis that lithium tritammonium is a chemical individual on the facts: (i) Lithium imide is easily decomposed on exposure to sunlight, according to the equation: $2Li_2NH=Li_3N+LiNH_2$, at the same time becoming coloured intensely red as shown by R. C. Mentrel. Trilithium amide is not sensitive to sunlight and therefore cannot be a mixture of lithium imide and lithium hydride; (ii) the conversion of Li_3NH_4 into Li_3NH_2 is a reversible process; (iii) analogy with tricalcium amide is not in favour of trilithium amide being a mixture of lithium amide and hydride. When the alleged lithium tritammonium is heated to 480°, **lithium tritamide,** Li_3NH_2, is formed. It possesses properties analogous to those of the triammonium compound. Lithium tritamide is also formed directly by the action of hydrogen on crystallized lithium nitride which has been obtained by heating lithium at 460° in a current of nitrogen; the reaction is so vigorous that the amide is obtained as a fused mass. When the tritamide is exposed to sunlight, a red substance, thought to be **lithium imide,** Li_2NH, is formed: $Li_3NH_2=Li_2NH+LiH$. Lithium tritamide, at about 600°, reacts with nitrogen, forming the imide: $4Li_3NH_2+N_2=6Li_2NH+H_2$. A. Guntz and F. Benoit gave 52·6 Cals. for the heat of formation of lithium imide.

E. C. Franklin prepared **rubidium diamidolithiate,** $Rb[Li(NH_2)_2]$, or $LiNH_2.RbNH_2$; **rubidium diamidosodiate,** $Rb[Na(NH_2)_2]$, or $NaNH_2.RbNH_2$; **rubidium triamidosodiate,** $Rb_2[Na(NH_2)_3]$; **potassium triamidolithiate,** $K_2[Li(NH_2)_3]$; and **potassium triamidosodiate,** $K_2[Na(NH_2)]_3$. As indicated above, lithium imide was reported by R. C. Mentrel to be formed by heating lithium amide to 450° in vacuo; but it is not formed by heating lithium and lithium amide in vacuo at 460°. O. Ruff and H. Georges obtained the imide by heating the amide in a silver dish at 360° until the evolution of ammonia had almost ceased, and then raising the temp. to 450°. It forms a white, partly-sintered mass of sp. gr. 1·303 at 19°; and it does not melt at 600°, but assumes a yellow colour—the white colour is restored on cooling. At higher temp., it decomposes, giving the blue lithium ammonia compound and a white powder—possibly lithium nitride. F. W. Dafert and R. Miklauz observed that on exposure to sunlight, lithium imide decomposes according to the equation: $2Li_2NH=Li_3N+LiNH_2$, the reaction being accompanied by the development of a dark red colour. At 450°, lithium imide reacts with hydrogen, forming the tritamide: $3Li_2NH+2H_2=2Li_3NH_2+NH_3$.

Attempts by A. W. Titherley to make **sodium imide,** Na_2NH, by the action of ammonia on sodium oxide gave sodamide, $NaNH_2$, and water: $Na_2O+2NH_3 \rightarrow 2NaNH_2+H_2O$. The water at once decomposes the sodamide, forming sodium hydroxide and ammonia, but if the action be suddenly stopped some of the primary product—sodamide—can be obtained; sodium oxide and sodamide do not react to any appreciable extent. See potassium and sodium amides for the properties.

F. F. Fitzgerald[3] treated a soln. of copper tetramminonitrate with potassium amide, and washed the olive-green precipitate. The product is thought to be **cuprous amide.** It is soluble in an excess of the alkali amide. E. C. Franklin treated cuprous nitride with a soln. of potassium amide in liquid ammonia, and obtained **cuprous hemipentamminopotassioamide,** $CuNK_2.2\frac{1}{2}NH_3$, or potassium ammoniocuprite, in colourless crystals which readily form **cuprous potassium amminoamide,** $CuNK_2.NH_3$, when heated below 200°, and at 200° form **cuprous potassium amide,** $CuNK_2$, or **potassium triamidocuprite,** $CuNK_2.2NH_3$ or $Cu(NH_2).2KNH_2$ or $K_2[Cu(NH_2)_3]$. E. C. Franklin mixed soln. of potassium amide and silver nitrate or iodide in liquid ammonia, and obtained a white precipitate of **silver amide,** $AgNH_2$. The compound is very explosive; it blackens in light; and is soluble in soln. of ammonium salts or of potassium amide in liquid ammonia, but not in the corresponding soln. of silver nitrate. J. Eggert showed that the sensitiveness of silver amide to explosion is not materially changed by lowering the temp. to —190°. A gradual isothermal change of press. to 5000 atm. brings about a decomposition of 97 per cent. of the samples of silver amide. E. C. Franklin found that **silver potassium amide,** $AgNHK.NH_3$, or $AgNH_2.KNH_2$, or $K[Ag(NH_2)_2]$, **potassium amidoargentate,** $AgNH_2+KNH_2=NH_3+AgNHK$, separates in crystals from conc. soln. of silver and potassium amides in liquid ammonia. These can be heated at 100° without change, but gradually undergo decomposition when left in the air. If the salt is treated with soln. of acids in liquid ammonia, silver amide is first precipitated, and dissolves, on further addition of the acid, with formation of the silver salt of the acid used. For **silver imide,** Ag_2NH, *vide* fulminating silver—**3.** 22, 11. According to J. Jacobsen, when silver nitrate is added to a soln. of chloroauric acid, a brown precipitate is obtained according to the equation $HAuCl_4+4AgNO_3+3H_2O=Au(OH)_3,4AgCl+4HNO_3$. By the action of ammonia, this is converted into fulminating gold, or **auric dihydroxyamide,** $Au(OH)_2.NH_2$, or $(AuN,2H_2O),H_2O$. The substance, when washed with aq. ammonia, followed by water, alcohol, and ether, and dried at a low temp., explodes violently when touched with a knife. The explosion takes effect in a downward direction. On boiling fulminating gold with potassium hydroxide, blackish-brown, flocculent, explosive, **auric tetrahydroxyimide,** $Au(OH)_2.NH.Au(OH)_2$, is formed. For F. Raschig's **auric imidoamide,** $NH : Au.NH_2$, and **auric chloroimide,** $NH : AuCl$, *vide* fulminating gold—**3.** 23, 14.

H. Moissan[4] prepared **calcium amide,** $Ca(NH_2)_2$, in transparent crystals, by the spontaneous decomposition of calcium ammine in an atm. of ammonia, or in a sealed tube. G. Roederer obtained white **strontium amide,** $Sr(NH_2)_2$, by heating the hexammine in vacuo at 50°, or by heating strontium in gaseous ammonia at 200°; at a higher temp., say 800°, only the hydride and nitride are formed. The Badische Anilin- und Soda-fabrik passed ammonia into soln. of the alkaline earth metals in fused, anhydrous alkali hydroxide. J. A. Joannis obtained **barium amide,** $Ba(NH_2)_2$, by allowing a mixture of barium bromide, potassium, and an excess of liquid ammonia to stand for some days; $BaBr_2+2KNH_3=2KBr+H_2+Ba(NH_2)_2$; H. Moissan, by the action of ammonia on barium hydride: $BaH_2+2NH_3=2H_2+Ba(NH_2)_2$; A. Guntz and R. C. Mentrel, by heating barium at 280°–400° in a stream of ammonia—above 460°, barium nitride is formed; and R. C. Mentrel, by warming barium hexammine—the reaction is slow at 0°, fast at 30°, and very rapid at 60°; and the reaction also proceeds more quickly in vacuo. The greyish-white barium amide is decomposed by moist air and by water. A. Guntz gave for the heat of formation: $Ba+2NH_3=Ba(NH_2)_2+H_2+53{\cdot}3$ Cals. For the properties, see the alkali amides.

According to F. W. Dafert and R. Miklauz, when a mixture of equal vols. of hydrogen and nitrogen is passed over the heated alkaline earth metals, or over their hydrides or nitrides, as the case may be, **calcium imide,** $CaNH$, **strontium imide,** $SrNH$, or **barium imide,** $BaNH$, is produced. These compounds darken on exposure to light as in the case of lithium imide. Calcium imide is the most easily prepared, but it has not been obtained pure ; while the formation of barium imide is incomplete. A. Guntz and F. Benoit gave 80·24 Cals. for the heat of formation of barium amide ; 84·3 Cals., for strontium amide ; 93·0 Cals., for calcium amide ; and for barium imide, $BaNH$, 54·4 Cals. E. C. Franklin prepared **potassium amidobariate,** $BaNK.2NH_3$, or $Ba(NH_2)_2KNH_2$, or $K[Ba(NH_2]_3]$, by the action of an excess of a barium salt on potassium amide, in liquid ammonia soln.; **potassium triamidocalciate,** $K[Ca(NH_2)_3]$, or $CaNK.2NH_3$; and **potassium diamidostrontiate,** $SrNK.2NH_3$, or $K[Sr(NH_2)_3]$, were made in a similar way.

According to F. W. Dafert and R. Miklauz, when calcium nitride is heated, within certain limits of temp., in a stream of hydrogen, the gas is absorbed, forming lemon-yellow or orange-yellow **calcium tritadiamide,** $Ca_3(NH_2)_2$, which is scarcely affected by heating in nitrogen or hydrogen, but changes slowly in diffused light, and rapidly in sunlight, to a greyish-black substance, probably a mixture of calcium imide and calcium hydride, formed according to the equation $Ca_3(NH_2)_2=2CaNH+CaH_2$. The amide, in an impure form, has also been prepared by heating calcium hydride in nitrogen. F. W. Dafert and R. Miklauz similarly obtained **strontium tritadiamide,** $Sr_3(NH_2)_2$, by the action of hydrogen on strontium nitride ; but **barium tritadiamide,** $Ba_3(NH_2)_2$, cannot be so obtained because it reacts with hydrogen. The temp. at which hydrogen and nitrogen unite with the metals and at which hydrogen unites with the nitride, are :

	Ca	Sr	Ba	Ca_3N_2	Sr_3N_2	Ba_3N_2
Nitrogen	410°	380°	260°	—	—	—
Hydrogen	300°	215°	170°	230°	270°	300°

This shows that the tendency of the alkaline-earth metals to combine with nitrogen and hydrogen increases with the at. wt., whilst the tendency of the nitrides to combine with hydrogen decreases with increase in at. wt. of the metal.

E. C. Franklin,[5] and F. W. Bergstrom prepared **magnesium amide,** $Mg(NH_2)_2$, by the action of magnesium on a soln. of the alkali metals in liquid ammonia; of sodium or potassium ammonomagnesiates on magnesium and liquid ammonia; and of lithium or sodium amide and magnesium on a soln. of sodium in liquid ammonia. F. W. Bergstrom obtained **magnesium diamminosodamide,** $Mg(NHNa)_2.2NH_3$, or $Na_2[Mg(NH_2)_4]$. He prepared **magnesium diamminopotassamide,** $Mg(NHK)_2.2NH_3$, or *potassium ammonomagnesiate*, by the action of potassium amide in liquid ammonia soln. on magnesium: $Mg+2KNH_2+2NH_3=H_2+Mg(NHK)_2.2NH_3$; or on magnesium iodide, nitrate, or acetamide: $MgI_2+4KNH_2=Mg(NHK)_2.2NH_3+2KI$. The salt occurs as a fine, crystalline powder, which is only slightly soluble in liquid ammonia, and is rapidly hydrolyzed by liquid water or water vapour. It is not explosive, and may be heated to 100° without loss of ammonia. For the properties, see the alkali amides. E. Frankland passed ammonia into an ethereal soln. of zinc ethyl, and obtained **zinc amide,** $Zn(NH_2)_2$, and ethane: $Zn(C_2H_5)_2+2NH_3=Zn(NH_2)_2+2C_2H_6$. The white, amorphous solid is not decomposed at 200° ; it is insoluble in ether ; and is decomposed by water : $Zn(NH_2)_2+2H_2O=2NH_3+Zn(OH)_2$. H. Peltzer said that with dry hydrogen chloride, ammonium tetrachlorozincate, $(NH_4)_2.ZnCl_4$, is formed. F. F. Fitzgerald, and E. C. Franklin prepared **zinc potassamide,** or **potassium tetramidozincate,** $K[Zn(NH_2)_4]$, $2KNH_2Zn(NH)_2$, or $Zn(NHK)_2.2NH_3$, by the action of a soln. of potassium amide in liquid ammonia on powdered zinc, zinc amide, or zinc tetramminoiodide for 7 days: $Zn(NH_3)_4I_2+4KNH_2$

$=Zn(NHK)_2.2NH_3+2KI+4NH_3$. The colourless crystals decompose on exposure to air; they react vigorously with water, forming ammonia, and zinc and potassium hydroxides; they are sparingly soluble in liquid ammonia, but soluble in soln. of ammonium salts in liquid ammonia; they dissolve energetically in dil. acids with the evolution of much heat; and they are not decomposed when heated to 160° in vacuo, but at a higher temp., they give off ammonia. If heated to 220°, **zinc amminopotassamide,** $Zn(NHK)_2.NH_3$, or $Zn(NH_2)_2.K_2NH$, **zinc potassium imidoamide,** is formed; and at 250°–325°, **zinc hemiamminopotassamide,** $Zn(NHK).\frac{1}{2}NH_3$, or potassium ammoniozincate. G. S. Bohart found that when cadmium iodide, or potassium cadmium cyanide, is treated with a soln. of potassamide in liquid ammonia, cadmium amide or potassium cadmium amide is formed according as the ammonio-base or the salt is in excess. **Cadmium amide,** $Cd(NH_2)_2$, is a white powder, which on exposure to moist air assumes an orange colour, and then slowly changes to pure, white cadmium hydroxide. It reacts violently with water, and when suddenly heated explodes with the liberation of metallic cadmium. When heated at 180° in vacuo, it loses ammonia and leaves cadmium nitride, Cd_3N_2, a black, amorphous powder, which becomes orange-coloured on exposure to moist air, and then slowly becomes white. It explodes violently when brought into contact with water, and deposits metallic cadmium. **Cadmium potassamide,** or *potassium cadmium amide,* $Cd(NHK)_2,2NH_3$, or **potassium tetramido-cadmiate,** $K[Cd(NH_2)_4]$, is a white, flocculent powder, which becomes grey when exposed to light. It reacts violently with water, producing ammonia, potassium hydroxide, and cadmium hydroxide. E. C. Franklin prepared **cadmium diamminopotassamide,** $Cd(NHK)_2.2NH_3$, *potassium ammoniocadmiate,* by adding potassium amide to a soln. of cadmium iodide or nitrate in liquid ammonia. For *mercury amide,* $Hg(NH_2)_2$; *mercury imide,* HgNH, and various derivatives—*vide* **4.** 31, 8 *et seq.* O. Ruff and E. Geisel found that soln. of mercuric iodide and nitrogen sulphide reacted in liquid ammonia soln., forming a precipitate of **mercuric thiodiimide,** $HgN_2S.NH_3$, in bright yellow crystals which resemble the lead compound, but contains one atom of sulphur less. The addition of lead iodide to the filtrate from the mercury compound produces a precipitate of lead dithiodi-imide, and, conversely, mercuric iodide precipitates mercury thiodi-imide from the filtrate from the lead compound. H. Hirzel obtained **mercurous amidoarsenate,** $Hg_2(NH_2)AsO_4$, by boiling mercuric oxide with a soln. of ammonium arsenate. The white compound resembled the corresponding amidophosphate. E. C. Franklin represented its constitution $Hg : AsO_4.Hg.NH_2$.

J. A. Joannis[6] prepared **boron amide** or **boramide,** $B(NH_2)_3$, by the action of ammonia on boron trichloride, at —23°: $BCl_3+15NH_3=3NH_4(NH_3)_3Cl+B(NH_2)_3$; and at 0°: $BCl_3+6NH_3=3NH_4Cl+B(NH_2)_3$. If the temp. be higher than this, the amide passes into the imide. The removal of the ammonium chloride by washing with liquid ammonia is attended by great losses. The preparation of **boron imide** or **borimide,** $B_2(NH)_3$, was effected by J. A. Joannis as just indicated, or by the action of ammonia on boron tribromide at 0°: $2BBr_3+27NH_3=6NH_4(NH_3)_3Br+B_2(NH)_3$. A. Stock and M. Blix made it by warming boron hexamminosulphide, $B_2S_3.6NH_3$, for many hours, at 115°–120°, in a current of dry hydrogen or ammonia: $B_2S_3.6NH_3=3NH_4SH+B_2(NH)_3$. The product is contaminated with a little sulphur, and in order to keep the amount small, the imide is powdered and treated with ammonia for a day at 115°. The white powder begins to give off ammonia above 125°, and at higher temp., the nitride is formed quantitatively: $B_2(NH)_3=2BN+NH_3$. The imide is insoluble in alcohol, ether, carbon disulphide, and liquid ammonia; no solvent is known which does not decompose the imide. Water decomposes it with the evolution of heat, forming boric acid and ammonia. The imide reacts with hydrogen chloride with the evolution of heat and the formation of **boron imidohydrochloride,** $B_2(NH)_3.3HCl$. After shaking boron imide for 12 hrs. with liquid ammonia, the imide increases in vol. and some amide is formed; if sulphur be mixed with the liquid ammonia, the imide, at 100°, acquires a dark blue colour, and on evaporation, an amorphous substance is formed which imparts to water a violet colour ; acids cause the separation of milk of sulphur.

F. W. Bergstrom [7] found that amalgamated aluminium reacts with sodamide in liquid ammonia soln., forming crystalline **sodium aluminium amide,** or *sodium ammonaluminate,* or *sodium amidoaluminate,* to which one of the following formulæ is applicable: $Al(NH_2)_2.NHNa.NH_3$; or $Al(NH_2)_3.NaNH_2$; or $Na[Al(NH_2)_4]$. The reactions are supposed to be $Al+3NaNH_2 \rightleftharpoons Al(NH_2)_3+3Na$; $Al(NH_2)_3+NaNH_2 = Al(NH_2)_2NHNa.NH_3$; and $3Na+3NH_3=\frac{3}{2}H_2+3NaNH_2$. This compound loses a mol of ammonia when heated in vacuo above 90°. The reaction with potassamide, forming **potassium aluminium amide,** $Al(NH_2)_2.NHK.NH_3$, or $Al(NH_2)_3.KNH_2$, is similar. It is assumed that dil. soln. of the alkali metals in ammonia are salt-like in character. If the product be dried in vacuo at 80°–115°, there remains potassium aluminium amide, $Al(NH_2)_2.KNH$. E. C. Franklin found that when an excess of aluminium iodide is added to a soln. of potassium amide in liquid ammonia, a white precipitate is produced which is redissolved by an excess of potassium amide; on the addition of potassium amide in quantity just sufficient to yield a permanent precipitate, **aluminium iodoamide,** or *ammoniobasic aluminium iodide,* is formed: $2AlI_3+3KNH_2 = 3KI+Al(NH_2)_3.AlI_3$. At ordinary temp., this salt separates from the soln. as a crystalline *hexammine,* $Al(NH_2)_3.AlI_3.6NH_3$; and at low temp., as an *octodecammine.* If potassium amide be added to a soln. of this salt in liquid ammonia, the composition of the precipitated salt is $Al(NH_2)_3.Al(NH_2)I.NH_3$; and when heated, it loses 2 mols of ammonia, forming $Al(NH_2)_3.AlNHI$, **aluminium iodoimidoamide.**

E. C. Franklin showed that if potassium amide acts on black thallium nitride in liquid ammonia, **thallous tetramminopotassioamide,** $TlNK_2.4NH_3$, or $TlNH_2.2KNH_2.2NH_3$, *potassium triamidothallite,* $K_2[Tl(NH_2)_3]$, is formed in golden-yellow crystals freed from excess of ammonia in vacuo at —40°. It loses 2 mols of ammonia at 20° in vacuo forming $TlNK_2.2NH_3$, or $TlNH_2.2KNH_2$; and at 100°, another $\frac{2}{3}$ mol, forming $TlNK_2.1\frac{1}{3}NH_3$, or $Tl_3N.6KNH_2$, or a mixture $Tl_3N+6KNH_2$. The crystals of the tetrammine are isomorphous with those of potassium amide, but *thallium amide and imide* are unknown in the free state, even at —33°. Both thallous nitride and the complex amides explode with great violence when subjected to shock, or heat, or when treated with water or dil. acids.

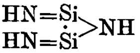
For *carbon amide,* see **2.** 20, 34. A. Stock and K. Somiesky [8] found that chlorosilane and ammonia gases react at ordinary temp., and if the former is in excess, ammonium chloride and **trimonosilylamine,** or **trisilylammonia,** $N(SiH_3)_3$, is formed as a spontaneously inflammable liquid: $3SiH_3Cl+4NH_3=(SiH_3)_3N+3NH_4Cl$. The vap. density agrees with the simple formula $N(SiH_3)_3$. The sp. gr. of the solid is 0·895 at —106° ; the b.p. is 52° ; and the m.p., —105·6°. The vap. press., p mm., is :

	—80°	—40°	—24·4°	—11·0°	—4·2°	0°	5°	10°	15°
p .	0·1	10	29	65	89	109	137	172	212

or $\log p = -1956·10T^{-1}+1·75 \log T - 0·00830T + 7·20404$. The liquid is stable in the absence of air ; it is vigorously decomposed by water: $N(SiH_3)_3+6H_2O = 3SiO_2+NH_3+9H_2$; it does not combine with hydrogen chloride or monochlorosilane ; but with hydrogen chloride: $(SiH_3)_3N+4HCl=3SiH_3Cl+NH_4Cl$. A homogeneous substance could not be isolated from the product of the action of monochlorosilane on an excess of ammonia. The chlorine is converted into ammonium chloride, and the silicon furnishes in the form of volatile compounds. The initial product is principally **disilylamine,** or **disilylammonia,** $NH(SiH_3)_2$, admixed with the tri- and mono- amines. The diamine is not stable in the dil. gaseous state, and slowly decomposes: $NH(SiH_3)_2=SiH_4+SiH_2:NH$, and the latter immediately condenses to the polymeric form $(SiH_2:NH)n$. The same product is obtained as a result of the reaction between dichlorosilane and an excess of ammonia: $SiH_2Cl_2+3NH_3=2NH_4Cl+SiH_2:NH$. The polymeride, $(SiH_2:NH)n$, is a white substance resembling silicic acid. The solid product in benzene soln. has n between 7 and 8. The residue obtained by evaporating the solvent is a viscid liquid which gradually passes into the solid—presumably a more highly polymerized condition. The polymeride is decomposed by a soln. of sodium hydroxide: $SiH_2:NH+2H_2O=SiO_2+2H_2+NH_3$, and the same change is more slowly produced by water; and with hydrogen chloride, $(SiH_3)_2NH+3HCl=2SiH_3Cl+NH_4Cl$. The behaviour towards gaseous hydrogen chloride is remarkable; mono-, di-, and tri-silylamines are smoothly and quantitatively transformed into monochlorosilane and ammonium chloride. The ready replaceability of the Si-N group by Si-halogen appears to be quite general with silicon compounds. In general, the compounds containing nitrogen exhibit a close analogy to the corresponding substances containing oxygen. Thus, the conversion of $NH_2.SiH_3$ into $NH(SiH_3)_2$ in the presence of an excess of ammonia is paralleled by the formation of $O(SiH_3)_2$, and not $SiH_3.OH$ by the action of an excess of water on monochlorosilane; the conversion of the volatile unimolecular SiH_2O into $(SiH_2O)x$ is similar to that of $SiH_2:NH$ into $(SiH_2:NH)x$, and affords a further example of the remarkable tendency towards polymerization of substances which contain but few hydrogen atoms directly united to silicon. O. Ruff and K. Albert prepared **silicon nitridihydride**, $H.Si:N$, by the action of ammonia on silicochloroform: $SiHCl_3+4NH_3=3NH_4Cl+SiHN$. O. Ruff found that the product is mixed with a little amide. On passing dry gaseous ammonia mixed with hydrogen into a Woulfe's bottle, cooled at 15°, into which silicochloroform diluted with hydrogen is simultaneously led, a white powder having the composition $N:SiH+3NH_4Cl+0{\cdot}2NH_3$ is obtained; the ammonium chloride may be almost completely removed by washing the product with liquefied ammonia in an apparatus from which moisture is excluded; but attempts to remove the ammonia completely, either at the ordinary temp. in a vacuum, or at 100°, cause partial decomposition according to the equation $SiNH+NH_3=Si(NH)_2+H_2$. The nitrohydride is a white powder with a caustic taste, which is decomposed by water or sodium hydroxide soln., giving hydrogen, thus: $SiHN+4NaOH=Si(ONa)_4+NH_3+H_2$; the action is quantitative. It has all the reducing properties of silicoformic anhydride, and is converted by dry hydrogen chloride at 300° into silicochloroform and ammonium chloride.

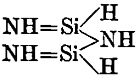
According to E. Lay, if a soln. of silicon tetrachloride in benzene be mixed with an emulsion of hydrazine in dry benzene, a white powder is obtained which is a mixture of crystals of hydrazine dichloride, and amorphous grains of a substance with the empirical composition, $Si(NH)_4$, or $Si(N_2H_2)_2$. A separation with organic solvents is not possible.

F. Lengfeld prepared **silicon tetramide**, $Si(NH_2)_4$, by the action of benzene soln. of silicon tetrachloride and ammonia, and subsequently evaporating the solvent. E. Vigouroux and C. Hugot allowed dry ammonia and silicon tetrachloride to react at −50°; much heat is developed. The ammonium chloride formed in the reaction is removed by washing the liquid ammonia on a glass-wool filter. Water decomposes the product with the evolution of ammonia. The white powder is stable below 0°; above that temp., ammonia is given off, and **silicon diimide**, $Si(NH)_2$, is formed. The diimide is formed by heating the tetramide at 120° or in vacuo at 100°. M. Blix made it by heating silicothiourea; some ammonium hydrosulphide is formed at the same time, but no free sulphur. M. Blix and W. Wirbelauer made it by the action of liquid ammonia on silicon disulphide, or silicon dichlorosulphide. In the latter case, the product is contaminated with some free sulphur. They also made it by treating silicon hexamminotetrachloride with liquid ammonia under press. The ammonium chloride was washed out with liquid ammonia. L. Gattermann employed a somewhat similar process. The white amorphous powder is stable even at the softening temp. of glass; but at a high temp., 900°, it is converted into silicam (*q.v.*). It is decomposed by moist air, and with water it furnishes silicic acid and ammonia. It does not furnish the amide when heated with ammonia. It forms salts with the halogen acids—*e.g.* liquid hydrogen chloride furnishes *silicon* *diimidodihydrochloride*, S.$(NH)_2.2HCl$. According to R. Schwarz and W. Sexauer, when a soln. of silicon hexachloride in anhydrous ether is gradually added to liquid ammonia, a polymer of **silicon diamidodiimide,** $NH_2.Si(NH).Si(NH).NH_2$, is formed, the accompanying ammonium chloride is removed by washing with liquid ammonia, and subsequently drying in a current of nitrogen at —20° to remove adsorbed ammonia. At about —10°, the compound loses ammonia, forming a polymer of **silicon triimide :**



$$\begin{array}{l} HN{=}Si \\ HN{=}Si \end{array}\!>NH$$

The triimide is stable at atm. temp. ; it decomposes above 400°, chiefly with the rupture of the silicon bridge, and the formation of some silicocyanogen, Si_2N_2. These compounds are very sensitive to oxygen, and particularly to moisture. A. Stock and F. Zeidler obtained **silicon dihydrotriimide :**



$$\begin{array}{l} NH{=}Si{<}^{H} \\ \quad\quad\quad >NH \\ NH{=}Si{<}_{H} \end{array}$$

by the action of ammonia on trichlorosilane under reduced press. and at ordinary temp., $2SiHCl_3+9NH_3=6NH_4Cl+[SiH(NH)]_2NH$. If the product be gradually heated it decomposes, mainly in accord with $[SiH(NH)]_2NH=2SiNH+NH_3$, and at about 250°, the ammonium chloride begins to sublime. The main action with hydrogen chloride is symbolized: $[SiH(NH)]_2NH+9HCl=2SiHCl_3+3NH_4Cl$. The action of ammonia on silicon tetrachloride furnishes **silicon imidodiamide,** $Si(NH_2)_2NH$, in accord with: $SiCl_4+7NH_3=4NH_4Cl+Si(NH_2)_2:NH$. M. Blix passed dry ammonia into a benzene soln. of silicon dibromosulphide, and obtained **silicon diamidosulphide,** $SiS(NH_2)_2$, or *silicon thiourea*, as a white powder which, after some time, decomposes: $SiS(NH_2)_2+2H_2O=SiO_2+H_2S+2NH_3$. It is decomposed by water into silicic acid, ammonia, and hydrogen sulphide. It has basic properties and forms salts with the halide acids. E. C. Franklin and T. B. Hine prepared **silicon potassioamidonitride,** $N{:}Si.NHK$, by the action of potassium amide, in liquid ammonia soln., on silicon amide.

A. W. Titherley obtained a brown powder by heating amorphous silica and alkali amide to 300°–400°. He regarded it as silicon imide. It was not decomposed by water or boiling alkali-lye; but with fused alkali-lye, ammonia is given off and alkali silicate formed.

M. Blix and W. Wirbelauer prepared **silicam,** or **silicon imidonitride,** Si_2N_3H, or NSi—NH—SiN, by heating silicon diimide to 900° in an atm. of dry nitrogen. Silicam was made in 1857, by H. St. C. Deville and F. Wöhler, by the action of ammonia on silicon tetrachloride. E. Lay made it by the action of dry ammonia on silicon hexamminotetrabromide, at 900°; an impure product is produced by heating it in hydrogen or nitrogen at 1000°. E. Lay found that the voluminous white powder so formed has no taste or smell; it has a sp. gr. of 2·015 at 17°; its colour is not changed by heating, but in the blue gas flame it slowly oxidizes with a greenish-yellow phosphorescence. The heat of formation is 132·44 Cals. When silicam is oxidized by heating it in *air*, nitrogen is evolved, but no apparent combustion occurs; in *oxygen*, however, combustion does occur with vivid incandescence—nitrogen and water are formed. If the oxygen be nascent—*e.g.* if the silicam be admixed with *lead dioxide; potassium chlorate, bromate, or nitrate; sodium dioxide; molybdic or chromic acid*—much of the nitrogen may be oxidized to nitrogen peroxide. Many oxides—*bismuth, cadmium, lead, copper, or mercury oxide*—are reduced when heated with silicam. M. Blix and W. Wirbelauer said that silicam is not decomposed by *water*, but E. Lay reported it to be slowly decomposed by water at ordinary temp., forming ammonia; with boiling water, the decomposition is rapid and complete. Boiling *alkali-lye* dissolves it, forming alkali silicate and ammonia; molten alkali hydroxide decomposes silicam very quickly.

Silicam is very stable towards the *halogens ;* with *chlorine* at a bright red-heat it forms hydrogen chloride. With *hydrofluoric acid,* silicam forms a clear soln. of ammonium fluosilicate. When heated with conc. *sulphuric acid,* ammonium sulphate is formed. When heated in a current of nitrogen at 1200°–1400°, it forms silicon nitride. Conc. *nitric acid* has no apparent action on silicam. When heated with *arsenic or antimony trioxide,* the metal and hydride are formed: $4As_2O_3+3Si_2N_3H=AsH_3+7As+6SiO_2+9N$. At a bright red-heat, silicam reduces *carbon dioxide* to carbon.

According to M. Blix and W. Wirbelauer, impure **titanium tetramide,** $Ti(NH_2)_4$, is produced by the action of liquid ammonia on titanium tetramminotetrachloride. A. Stähler obtained the same product by the action of liquid ammonia on the hexamminotetrachloride or octamminotetrachloride. The compound is vigorously decomposed by water. When the amide is heated, M. Blix and W. Wirbelauer say that **titanium diimide,** $Ti(NH)_2$, is probably formed. O. Ruff and F. Eisner said that the tetramide is always contaminated with chlorine, which on ignition furnishes hydrogen chloride, ammonium chloride, and **titanium chloronitride,** TiNCl. E. C. Franklin and T. B. Hine prepared **titanium potassioamidonitride,** $N:Ti.NHK$, by the action of potassium amide on titanium tetrabromide in liquid ammonia soln. The soln. probably contains the ammonolytic product **titanium bromonitride,** $N:TiBr$, which reacts: $N:TiBr+2KNH_2=KBr+NH_3+N:Ti.NHK$. The impure, brick-red powder is not explosive, but is vigorously decomposed by water. A. Stähler and B. Denk treated zirconium hexamminoiodide with liquid ammonia and obtained the octamminoiodide, which, when washed with liquid ammonia, decomposes into a mixture of **zirconium amide,** $Zr(NH_2)_4$, and ammonium iodide: $ZrI_4.8NH_3=4NH_4I+Zr(NH_2)_4$.

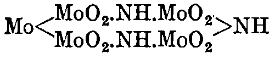
F. W. Bergstrom obtained **potassium stannous amide,** $Sn(NH_2)_2.KNH_2$, or $SnNK(NH_3)_2$, or $K[Sn(NH_2)_3]$, as a white solid, very soluble in liquid ammonia, by the action of mercury on the product of the reaction of tin with potassium amide; by the action of the amide on an excess of tin amalgam; or by the action of potassium amide on stannous chloride. The corresponding **sodium stannous amide,** $Sn(NH_2)_2.NaNH_2$, or $SnNaN(NH_3)_2$, or $Na[Sn(NH_3)_2]$, was obtained in a similar way. F. F. Fitzgerald found that when an excess of a soln. of potassamide in liquid ammonia is added to one of stannic iodide in the same solvent, a crystalline precipitate of **potassium stannic amide,** or *stannic tetramminopotassamide,* or *potassium hexamidostannate,* $K_2[Sn(NH_2)_6]$, or $Sn(NK)_2.4NH_3$, is produced, which, when heated at 145°, loses 3 mols. of ammonia. On further heating in a vacuum at 316°, a brick-red powder is obtained, which still contains some ammonia and is decomposed violently by water with evolution of gas and deposition of tin. E. C. Franklin showed that if a liquid ammonia soln. of potassium amide be treated with a soln. of lead iodide, an orange-red precipitate of **lead imide,** PbNH, is slowly formed. The colour slowly becomes brown. The compound explodes when heated, or when treated with water or dil. acids. It is dissolved by dil. acetic acid or dil. potash-lye. It is slowly decomposed by steam. If lead nitrate be used in place of the iodide, a basic salt, possibly $Pb_2N(NO_2)nNH_3$, is formed. With an excess of potassium amide a soluble **lead potassimide,** KPbN, is slowly formed. E. C. Franklin also made **potassium triamidoplumbite,** $K[Pb(NH_2)_3]$; and **lead iodoimidoamide,** $NH_2.PbNH.PbI$, or $Pb:N.PbI.NH_3$, or $PbNH.PbNH_2I$, by pouring potassium amide soln. on one of lead iodide and shaking the mixture as long as the lead iodide is in excess. The white, non-explosive precipitate, when heated, loses ammonia and gradually darkens in colour. Soln. of metal iodides in liquid ammonia were found by O. Ruff and E. Geisel to give precipitates with a liquid ammonia soln. of nitrogen sulphide; thus, lead iodide forms **lead dithiodiimide,** $PbN_2S_2.NH_3$, crystallizing in olive-green prisms, becoming orange in air without alteration of weight, decomposing when slowly heated, and exploding very violently at 140° when rapidly heated. Hydrogen chloride reacts quantitatively according to the equation $PbN_2S_2,NH_3+6HCl=PbCl_2+3NH_3+2S+4Cl$. Dry liquid hydrogen sulphide reacts thus: $PbN_2S_2,NH_3+3H_2S=PbS+4S+3NH_3$. Ethyl iodide forms ethyl sulphide and lead iodide. E. Chauvenet showed that when thorium tetramminotetrachloride is heated to 250°–300°, it forms **thorium amide,** $Th(NH_2)_4$, and at a red-heat, **thorium imide,** $Th(NH)_2$.

The amido- and imido-compounds of weak electronegative elements have not been prepared; no compounds of the NH_2-group with chromium, molybdenum, tungsten, and uranium are definitely known, but some more complex compounds of this type have been reported. R. J. Meyer and H. Best[9] obtained no evidence of the formation of **amidochromic acid,** $HO.CrO_2.NH_2$, by the action of ammonia on a soln. of potassium chlorochromate in dry acetone. E. Heintze prepared **potassium amidochromate,** $NH_2.CrO_2.OK$, by the action of dry ammonia on a soln. of potassium chlorochromate in dried ether free from alcohol. The aq. soln. of the salt furnishes red crystals which can be dried at 100°. J. Ohly also obtained it by the action of dry ammonia on potassium chlorochromate. A. Fock said that the monoclinic crystals have the axial ratios $a:b:c=1\cdot02832:1:1\cdot7751$. A cold, sat., aq. soln. contains 13 per cent. of the salt. If boiled for some hours with water, it is converted into a mixture of potassium and ammonium chromates; it reacts with nitrous acid: $2HNO_2+2K(NH_2)CrO_3=K_2Cr_2O_7+2N_2+3H_2O$; and when boiled with alkali-lye, ammonia is given off. Both G. Wyrouboff, and A. Werner and A. Klein were unable to prepare this compound by E. Heintze's method, and regard his product as impure potassium dichromate. S. Löwenthal prepared **ammonium amidochromate,** $(NH_4O)(NH_2)CrO$, by a process like that employed by E. Heintze for the potassium salt; and A. Fock described the monoclinic crystals. G. Wyrouboff, and A. Werner and A. Klein were unable to prepare the amidochromate, and G. Wyrouboff suggested that the alleged amidochromate is impure ammonium dichromate. S. Löwenthal obtained **lithium amidochromate,** $LiO.CrO_2.NH_2$, by the method employed for the potassium salt. A. Fock observed that the crystals are triclinic, but G. Wyrouboff could not obtain this compound when purified lithium salts were used. S. Löwenthal reported an impure **magnesium amidochromate,** and a **mercury amidochromate,** $Hg_3(CrO_3)_2NH_2$, formed by the action of potassium amidochromate on a soln. of mercuric acetate in conc. acetic acid. Some of the mercuriammonium chromates can be represented as amido-compounds. For the *amido-phosphates, vide* phosphorus. B. Skormin prepared **mercuric dioxydiamidochromate,** $3HgO.Hg(NH_2)_2.CrO_3$, or $Hg_4O_2(NH_2)_2CrO_4$, by the action of an excess of mercuric nitrate on ammonium chromate in a boiling soln.

A. Rosenheim and F. Jacobsohn treated freshly prepared potassium chlorochromate with liquid ammonia in a sealed tube. The product after washing with liquid ammonia corresponded with **potassium ammonium imidochromate,** $(NH_4)KCrO_3NH$, or $(KO)(NH_4O).CrO.NH$. When exposed to air, or when dissolved in water, ammonia is given off, and the ordinary chromate is formed. They also passed dry ammonia into a soln. of chromyl chloride in dry chloroform and obtained a brown voluminous mass with the composition $(NH_3)_3(CrO_2)_2(NH_4)_2$, which may be **ammonium triimidochromate,** $HN(NH.CrO.ONH_4)_2$. Most of the ammonium chloride can be washed away from the product by means of liquid ammonia. When chromic anhydride is treated with liquid ammonia in a sealed tube at ordinary temp., the product has the empirical composition $CrO_3.3NH_3$, but is thought to be **ammonium imidochromate,** $HN:CrO(ONH_4)_2$. The compound readily gives up ammonia to air, and dissolves in water to form ammonium dichromate. By the interaction of lead iodide, chromic anhydride, and liquid ammonia, **ammonium lead imidochromate,** $\{NH:CrO(ONH_4)O\}_2Pb$, is formed as a brown powder.

J. Ohly reported that he had made **chromyl amide,** or **chromium dioxyamide,** $CrO_2(NH_2)_2$, by dissolving potassium amidochromate in water; mixing with conc. aq. ammonia; covering the liquid with a layer of ether; and treating with chlorine. The brown soln. deposits leaflets of the alleged chromyl amide, which gives off ammonia when rubbed with soda-lime; and its aq. soln. gives the amido reactions with silver nitrate and lead acetate.

E. Uhrlaub prepared a substance with the composition $Mo_4N_{10}H_4$ and one with the composition $Mo_9N_{10}H_4$, by the action of dry ammonia on molybdenum chloride. The simpler formula *molybdenum imidonitride,* MoN_2H, may well apply. He also examined the action of dry ammonia on warm molybdenum trioxide, but the product was probably a mixture. The conclusions are therefore unsatisfactory. E. F. Smith and V. Lenher treated molybdenyl chloride, MoO_2Cl_2, with dry ammonia and obtained a substance with the composition $Mo_5O_8N_3H_3$, which they supposed to be **molybdyl triimide :**



$$Mo\begin{matrix}\diagup MoO_2.NH.MoO_2 \diagdown \\ \diagdown MoO_2.NH.MoO_2 \diagup\end{matrix}NH$$

Much heat is developed during the action, and ammonium chloride and water are formed. The compound has a black, metallic appearance, and is stable in the air; it does not combine with hydrochloric acid, but is energetically attacked by nitric acid (sp. gr. 1·42), slowly by dil. alkalis, and yields ammonia when fused with potassium hydroxide. When heated in an atm. of nitrogen, water is formed, and a red compound is obtained, which is probably molybdenum dioxide mixed with a small quantity of nitride. When treated with aq. silver nitrate, crystals of metallic silver are deposited. When molybdenyl chloride is heated to bright redness in an atm. of ammonia, an amorphous, black, metallic-looking mass is formed with the composition $Mo_7O_{14}N_5H_{10}$, **molybdyl pentamide**. It is not attacked by dil. alkalis, gives ammonia when fused with potassium hydroxide, is energetically converted into molybdic acid by the action of nitric acid, and precipitates silver from a soln. of silver nitrate. According to A. Rosenheim and H. J. Braun, when molybdenum trichloride is heated to 340° in ammonia, black **molybdenum triamidotrichloride,** $Mo_2(NH_2)_3Cl_3$, is formed—the ammonium chloride can be removed by washing with water since the amidochloride is insoluble in water and dil. acids. If kept for four days in a sealed tube with liquid ammonia, **molybdenum decamminotriamidotrichloride,** $Mo_2(NH_2)_3Cl_3(NH_3)_{10}$, it forms as a brown mass. The ammonium chloride can be removed by washing with liquid ammonia. When exposed to air, the decammine gives off ammonia, and when gently heated, it forms the triamidotrichloride. If molybdic chloride be treated with 25 per cent. aq. ammonia, the black, or dark green or brown mass has the empirical composition MoO_4NH_4, and corresponds with **molybdyl hydroxyamide,** $(NH_2)MoO_2(OH).H_2O$. H. Fleck and E. F. Smith obtained a similar product, $(NH_2)MoO_2(OH)$, by the action of dry or aq. ammonia on a chloroform soln. of molybdenyl chloride. The black precipitate—probably *molybdyl diamide,* $MoO_2(NH_2)_2$—forms the brownish-red hydroxyamide when extracted with alcohol. A. Rosenheim and F. Jacobsohn found that liquid ammonia reacts with molybdenum trioxide, forming a snow-white substance with the empirical composition $MoO_3.3NH_3$, **molybdenum triamminotrioxide,** and the same substance was formed by the action of liquid ammonia on molybdenyl chloride. The product was thought to be **ammonium imidomolybdate,** $NH:MoO(ONH_4)_2$; **ammonium lead imidomolybdate,** $(NH_4)_2Pb[Mo(NH)O_3]_2$, was also prepared. When a soln. of potassium amide in liquid ammonia acts on molybdenum trioxide, a mixture of $NH:MoO(OK)_2$, **potassium imidomolybdate,** and *potassium nitrilomolybdate* $NK:MoO(OK)_2$, appears to be formed. F. W. Bergstrom found that nitridation occurs when soln. of molybdenum halides in liquid ammonia are kept for some days. **Potassium ammoniomolybdite,** or **molybdenum amidodipotassimide,** $Mo(NK)_2NH_2$, is precipitated by adding excess of potassamide soln. to molybdenum tribromide soln., and keeping for some weeks. Free potassium is formed owing to reduction of the potassamide and " nitridation " of the molybdenum ; hydrogen and nitrogen are simultaneously formed. The compound reacts vigorously with water and is soluble in dil. sulphuric acid; it loses $0{\cdot}5NH_3$ at 120°–130° in a vacuum. The **sodium ammoniomolybdite,** or **molybdenum amidodisodimide,** is prepared using molybdenum pentachloride and sodamide.

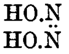
F. Wöhler reported a **tungsten imidonitride,** $W_3N_6H_4$, or $W(NH.W.N:NH)_2$, to be formed when ammonia is passed over heated tungsten hexachloride. The black mass appears like coke. When heated in air, ammonia is first evolved, and the mass then burns to tungsten trioxide. Acids, and alkali-lye are without action; molten potassium hydroxide forms a tungstate with the evolution of ammonia and hydrogen. It is reduced to metal when heated with carbon, hydrogen and nitrogen are evolved. Ammonia is given off when the compound is heated in hydrogen, and **tungsten imide,** $W(NH.W.NH)_2$, is formed with the evolution of ammonia. At a higher temp., the metal is produced. F. W. Bergstrom observed that **potassium ammoniotungstite,** or **tungsten amidodipotassimide,** $W(NK)_2NH_2$, is precipitated as above, using a soln. of potassamide and tungsten pentabromide in liquid ammonia. It is pyrophoric, blackens in air, and reacts violently with water. If excess of halide is used in these precipitations, ammonio-basic mixtures are obtained.

S. Rideal heated tungsten trioxide with ammonium chloride until its weight was constant. The composition corresponded with *tungsten oxynitride,* $WO_3.WN_2$, or $W_2N_2O_3$. E. D. Desi reported a number of oxynitrides to be formed in an analogous manner, $W_{20}N_{27}O_4$, W_2N_4O, $W_5N_6O_4$, etc. Both A. Lottermoser, and M. Guichard consider that the alleged oxynitrides are partially reduced tungstic oxide mixed with a nitrogen compound, and possibly elemental tungsten. F. Wöhler obtained what he regarded as *tungsten oxyamidonitride,* $W_7N_8H_4O_4$, or, according to S. Rideal, $W_9N_{10}H_4O_4$, by the action of dry ammonia on heated tungsten trioxide, or an excess of ammonium chloride on potassium tungstate followed by leaching with water. The black scales give off ammonia when heated; in hydrogen, ammonia and water are given off and the metal remains; in air, tungsten trioxide is formed. The compound is also oxidized when heated with copper oxide or red-lead. With sodium hypochlorite, hydrogen is given off. Water at 230°, acids, and alkali-lye do not act on the compound, but fused potassium hydroxide forms a tungstate with the evolution of ammonia. When tungsten trioxide is heated to dull redness in a current of dry ammonia, S. Rideal said that a grey amorphous powder with the composition $W_5N_6H_3O_5$, is formed. These substances are probably mixtures.

According to E. F. Smith and O. L. Shinn, a substance with the composition $W_4N_4O_4H_2$, is formed when tungstyl chloride, WO_2Cl_2, is heated in a current of dry ammonia. There is no action at ordinary temp. The black mass is insoluble in water, it is not attacked by hydrochloric acid or dil. alkalis, but is very energetically acted on by conc. nitric acid, and yields ammonia when fused with potassium hydroxide. It is not altered by heating with conc. sulphuric acid at 180°–250°. When treated with aq. silver nitrate, crystals of metallic silver are deposited. A. Rosenheim and F. Jacobsohn said that liquid ammonia does not react with tungsten trioxide even at 108°–109° in a sealed tube; with hydrated tungsten trioxide, liquid ammonia forms **tungsten diamminotrioxide,** $WO_3.2NH_3.H_2O$; and with tungstyl chloride, brown **tungsten triamminotrioxide,** $WO_3.3NH_3$.

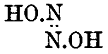
Uranium trioxide does not react with liquid ammonia, but uranyl chloride furnishes a greyish-green precipitate which has not been obtained pure. E. F. Smith and J. M. Matthews prepared **uranium oxynitride,** $U_{11}N_5O_{25}$, by heating uranyl chloride in a porcelain boat heated in a current of dry ammonia, when, at a comparatively low temp., the material assumes a dark colour, and copious fumes of ammonium chloride are evolved; the heat is then raised and continued until no more fumes are given off, and a dull black residue free from chlorine is left. This, when fused in a nickel crucible with potassium hydroxide, slowly evolves ammonia. When introduced into soln. of silver nitrate, brilliant crystals of metallic silver are formed. When heated in a sealed tube with dil. sulphuric acid (1–2), complete soln. ensues. V. Kohlschütter and K. A. Hofmann prepared the oxynitride, UO_5N, by dehydrating hydroxylamine uranate at 125° until the weight was constant; this is a brownish-black substance with metallic lustre; cold, dil. acids liberate a mixture of nitrogen and nitrous oxide, uranic acid remaining dissolved.

In 1894, J. Thiele and A. Lachman[10] prepared **nitramide,** or **nitroxyl amide,** $NH_2.NO_2$, *i.e.* $H_2N_2O_2$, isomeric with hyponitrous acid. They found that by adding a soln. of potassium hydroxide to a conc. aq. soln. of nitrourethane, $NO_2.NH.COOC_2H_5$, at 0°, potassium nitrocarbamate, $NO_2.NH.COOK$, separates in plates which are immediately decomposed by water with the development of heat yielding nitrous oxide and potassium carbonate; if, however, the potassium nitrocarbamate be treated with a mixture of ice and sulphuric acid, nitrocarbamic acid, $NO_2.NH.COOH$, is set free, and this at once splits up into carbon dioxide and nitramide, $NH_2.NO_2$. To isolate the nitrocarbamide, the soln. is sat. with ammonium sulphate, and extracted with ether; on evaporating the ether in a current of air at ordinary temp., the nitramide separates out in prismatic crystals, and if light petroleum be present in the ethereal soln., lustrous plates are formed. J. Thiele and A. Lachman also made it in small quantities by the action of potassium imidosulphonate in conc. sulphuric acid, on nitric acid or ethyl nitrate. Nitramide melts at 72°, but the m.p. is considerably lowered by traces of moisture. Nitramide is somewhat volatile at the ordinary temp., and dissolves in all the common solvents with the exception of light petroleum, the aqueous soln. having a strongly acid reaction. It is most unstable, and when mixed with copper oxide, lead chromate, or even glass powder, decomposes into nitrous oxide and water with development of heat. It is also decomposed by conc. sulphuric acid and by hot water, but, unlike the alkylnitramines, is equally unstable in alkaline soln. According to J. N. Brönsted and C. V. King, the decomposition of nitramide, $H_2N_2O_2 \rightarrow H_2O+N_2O$, is strongly catalyzed by platinum black, but not by bright platinum. The decomposition in water at 15° is 10 per cent. faster than the spontaneous decomposition in acid soln. at the same temp. The dissociation constant $K=2{\cdot}5\times10^{-7}$. On reduction, it yields a substance having strong reducing properties, probably hydrazine. E. Baur found the mol. conductivity, μ, of nitramide for a mol made up to 1·941 and 63·105 litres, to be between 0·5205 and 1·126; and, owing to decomposition, A. Hantzsch and L. Kaufmann found the latter value fell to 1·042. They also found for $v=32$ and 64, respectively $\mu=1{\cdot}95$ and 1·69, and consider nitramide to be an acid with a conductivity about 500 times smaller than that of acetic acid; E. Baur's results led him to conclude that the acid is 5–6 times weaker than acetic acid. A. Hantzsch measured the transport numbers of the ions, and concluded the strength of the acid is 40–50 times less than that of acetic acid. The salts are particularly unstable. J. N. Brönsted and co-workers found that the aq. soln. decomposes quantitatively: $H_2N_2O_2=H_2O+N_2O$; and is slow enough for measurement in dil. hydrochloric acid soln. at 15°. The reaction is accelerated in the presence of basic substances. J. Thiele and A. Lachman said that the *alkali nitramidates* can exist only for a few seconds; and the ethereal soln. of nitramide and an alcoholic soln. of ammonia furnish *ammonium nitramidate* which begins to give off gas immediately. J. Thiele and A. Lachman found *mercuric nitramidate*, $HgN.NO_2$, to be a little more stable. J. Thiele considered nitramide to be the true amide of nitric acid, and explained the formation of salts by the assumption that nitramide passes into the tautomeric *imidonitrous acid*, HN : NO.OH; on the other hand, A. Hantzsch did not accept the amide theory, but regarded nitramide as an acid *syn*diazohydrate, in contradistinction to the isomeric hyponitrous acid (*q.v.*) was considered to be *anti*diazohydrate.



$$\begin{array}{l}\mathrm{HO.N}\\ \mathrm{HO.\ddot{N}}\end{array}$$

Nitramide.



$$\begin{array}{l}\mathrm{HO.N}\\ \quad\;\mathrm{\ddot{N}.OH}\end{array}$$

Hyponitrous acid.

The phosphorus nitride of the early workers—H. Rose,[11] and F. Wöhler and J. von Liebig—was probably **phosphorus imidonitride,** PN_2H, or $N \vdots P : NH$, sometimes called **phospham.** It was made by F. Wöhler and J. von Liebig, C. Gerhardt, and H. Davy by heating phosphorus pentachloride in ammonia; and by H. Rose, by the action of ammonia on phosphorus pentachloride, trichloride, or tribromide: $5PCl_5+8NH_3=4PN_2H+17HCl+3H+P$. A. Besson made it by slowly heating phosphorus octamminopentachloride to 200°, and then finishing at 250°–300°; W. Couldridge, by the action of ammonia on phosphorus trinitrilohexachloride,

$P_3N_3Cl_6+3NH_3=P_3N_3(NH)_3+6HCl$; and R. Vidal, as a 90 per cent. yield, by heating a mixture of phosphorus pentasulphide and ammonium chloride. Phospham is a white, pulverulent solid. The analyses of C. Gerhardt, H. Rose, F. Wöhler and J. von Liebig, and A. Besson agree with the formula PN_2H; but the phospham prepared by A. Pauli, by the action of ammonium chloride on phosphorus pentasulphide or pentachloride, was probably impure; and the same remark applies to that prepared by M. Salzmann, by the action of ammonia on phosphorus pentachloride. Phospham can be regarded as a nitrile of phosphoric acid, H_3PO_4, formed by the abstraction of the equivalent of four mols of water from a mol of diammonium hydrogen phosphate, $(NH_4O)_2PO.OH$; phosphoryl nitrile, PON, may be regarded as derived from ammonium dihydrogen phosphate, $(NH_4O)PO(OH)_2$, by the abstraction of three mols of water; and a third nitrile would be formed by the abstraction of four mols of water from normal ammonium phosphate, $(NH_4O)_3PO$. This would furnish PN_3H_4, a compound which has not yet been reported. D. I. Mendeléeff regards phospham as a polymeride of PN_2H, analogous with hydrazoic acid or azoimide, N_3H, in agreement with the fact that both phosphorus and its compounds show a greater tendency to polymerization than nitrogen and its compounds. According to A. W. Hofmann, the non-volatility of phospham shows that it is a polymeride, probably $P_3N_3(NH)_3$, and this is in agreement with W. Couldridge's work—*vide supra.*

A. Besson found that the amide gives off ammonia when heated, and at a red-heat in vacuo, or in a stream of nitrogen, it forms phosphorus. Phospham, according to H. Rose, does not melt or volatilize, in a closed vessel protected from air, at a dull red-heat, but when heated in *air*, it forms white clouds of phosphorus pentoxide, and oxidizes slowly without inflammation. When heated in *hydrogen* it forms phosphorus and ammonia. C. Gerhardt heated phospham moistened with *water*, and found that it decomposes: $PN_2H+3H_2O=HPO_3+2NH_3$. H. Rose observed that it is not decomposed by dry *chlorine*, or dry hydrogen chloride; if moisture be present, ammonium chloride is formed. It is not dissolved or decomposed by dil. *hydrochloric acid.* F. Wöhler and J. von Liebig said that a mixture of phospham and *potassium chlorate* detonates when heated giving off chlorine. H. Rose observed that it is not decomposed in contact with molten or distilling *sulphur.* At a red-heat, dry *hydrogen sulphide* decomposes phospham, forming white clouds which condense to a white or yellowish-white powder.

This powder takes fire in air at a summer's heat, and burns with a white flame to form phosphoric acid; it is violently oxidized and dissolved by nitric acid, forming sulphuric and phosphoric acids; it inflames in the vapours of nitrogen peroxide; it has no odour when freshly prepared, but after exposure to air, it acquires the smell of hydrogen sulphide; it forms a turbid soln. when treated with water, which deposits sulphur and smells of hydrogen sulphide; it evolves ammonia when treated with alkali-lye; and it is dissolved by hot alkali-lye but not by aq. ammonia or hydrochloric acid. The product is probably a mixture of phosphorus sulphide, and ammonium salts.

Returning to phospham, H. Rose found that it is not dissolved or decomposed by dil. *sulphuric acid,* but it is dissolved by the conc. acid giving off sulphur dioxide and forming phosphoric acid. Phospham is not decomposed by dry *ammonia.* It is scarcely affected by dil. *nitric acid,* but the conc. acid slowly oxidizes it to phosphoric acid; and, added A. Pauli, it is not dissolved by fuming nitric acid. H. Rose found that a mixture of phospham and a *nitrate* detonates when heated. Phospham is not decomposed by dry *carbon dioxide,* and when heated with *alkali carbonates* it gives off carbon dioxide and ammonia, forming alkali phosphates —R. Vidal said that at a red-heat, cyanates are formed: $PN_2H+2M_2CO_3=M_2HPO_4+2MOCN$; and with *oxalates:* $PN_2H+M_2C_2O_4=M_2HPO_4+C_2N_2$. The vapour of *methyl* or *ethyl alcohol* at 150°–200° forms a phosphate of the primary amine: $PN_2H+4ROH=PO_4H(NH_2R_2)_2$ or $PO_4H(NH_2R_2)_2=ROH+R(NH_3)PO_3+NHR_2$; *propyl alcohol* gives propylamine and propyl oxide; *phenol,* diphenyl amine; *glycol* at 210° reacts: $2C_2H_4(OH)_2+PN_2H=(NH_4)_2HPO_4$

$+2C_2H_2$; *formic acid* at 150°–200° reacts: $PN_2H+2HCOOH=H_3PO_4+2HCN$; with the homologous *fatty acids*: $PN_2H+2RCOOH=H_3PO_4+2RCN$; and dioxy-compounds give diphenylamine derivatives. H. Rose found that phospham is decomposed by fused *potassium hydroxide* frequently with incandescence, forming nitrogen, hydrogen, ammonia, and alkali phosphate. Fused barium hydroxide acts similarly. Boiling alkali-lye does not decompose or dissolve phospham. F. Wöhler and J. von Liebig found that *mercuric oxide* decomposes phospham with incandescence, forming mercuric phosphate; *cupric oxide* acts similarly. F. W. Dafert and A. Uhl heated phospham with various oxidizing agents—*barium dioxide, lead chromate, lead dioxide, manganese dioxide, potassium permanganate, cupric oxide,* etc.—and found that *silver oxide* gave the most uniform results and also acted at a comparatively low temp. In these circumstances, exactly one-half of the nitrogen contained in phospham is eliminated in the form of nitrogen compounds, whilst the other half is evolved in the elementary condition. This is probably accounted for by the difference in the mode of linking of the nitrogen atoms in the phospham mol., $N \vdots P : NH$. Phospham is not greatly changed in the soil, and cannot serve as a source of nitrogen or phosphorus for plants.

The observations of G. Perpérot[12] indicate that when the ammine $PCl_3.6NH_3$ is heated, ammonium chloride and **phosphorus triamide,** $P(NH_2)_3$, are formed; and with the ammine, $PCl_5.10NH_3$, **phosphorus pentamide,** $P(NH_2)_5$. H. Perpérot represented the reaction with the phosphorus amminochlorides: $PCl_n+2nNH_3 \rightarrow PCl_n.2nNH_3 \rightarrow P(NH_2)_n+nNH_4Cl$. According to C. Hugot, liquid ammonia reacts with phosphorus tribromide a little below —70°, forming **phosphorus amide,** $P(NH_2)_3$, thus: $PBr_3+15NH_3=3NH_4(NH_3)_3Br+P(NH_2)_3$; most of the ammonium bromide can be removed by rapidly washing with liquid ammonia. If phosphorus triiodide be employed at about —65°, the amide, being soluble in the ammonium triamminoiodide, cannot be isolated. The yellow, amorphous amide is insoluble in a soln. of ammonium triamminobromide, but is soluble in the triamminoiodide; it slowly decomposes at 0° into brown **phosphorus imide,** $P_2(NH)_3$, thus, $2P(NH_2)_3=3NH_3+P_2(NH)_3$. J. A. Joannis obtained the imide by keeping the imidoamide between 0° and 100° for a few hours: $2NHPNH_2=NH_3+P_2(NH)_3$. C. Hugot observed that the soln. of the amide in ammonium triamminoiodide at —65° slowly deposits the imide. The brown imide slowly decomposes when heated; and this occurs rapidly in vacuo at 250°–300°, forming a red substance which does not decompose completely into nitrogen and phosphorus at a red-heat. The imide is insoluble in a soln. of ammonium triamminoiodide. According to R. Schenck, and A. Stock, **phosphorus imidoamide,** $H_2N.P : NH$, is probably formed as a by-product in the action of liquid ammonia on ordinary phosphorus. Yellow phosphorus, purified by distillation in a current of steam, is treated with liquid ammonia, gives off some hydrogen, and is converted into red phosphorus and small quantities of a hydride; an amide, imide, or probably phosphorus imidoamide, $NH_2.P : NH$, is formed at the same time. The hydride is said to unite with ammonia, forming a black mass which has the composition $(NH_4)P_4H$; and the reaction is accordingly symbolized: $14P+7NH_3=3P_4H(NH_4)+2NH_2PNH$. J. A. Joannis made it by passing dry hydrogen and phosphorus chloride vapour at liquid ammonia at —78°. The constancy of the proportions of imide: amide made it appear as if there was a complex formed, and at —23°, the reaction is represented: $PCl_3+14NH_3=3NH_4(NH_3)_3Cl+NH_2.P : NH$. It decomposes into the imide between 0° and 100°. Both the amide and imide have been used in the manufacture of incandescent lamp filaments by the Zirkon Glühlampenwerke.

By treating arsenic trichloride with ammonia, J. Persoz[13] obtained what he regarded as $AsCl_3.3NH_3$; H. Rose, $2AsCl_3.7NH_3$; and A. Besson, $AsCl_3.4NH_3$. The product is a pale yellow or white powder which, according to H. Rose, dissolves gradually in water with the evolution of heat, the loss of ammonia, and the formation of ammonium chloride; only a portion of the ammonia in the soln. is precipitated by hydrochloroplatinic acid. According to L. Pasteur, when heated, the product evolves ammonia, a portion then sublimes unchanged, and lastly, a sublimate of ammonium chloride is produced. When the soln. in cold water is evaporated, a substance, $As_4N_2Cl_2H_{10}O_7$, remains. This is probably a mixture of ammonium chloride, etc. Hot water decomposes the amminochloride into arsenic trioxide, ammonia, and ammonium chloride. According to J. von Liebig and F. Wöhler, the soln. formed with boiling alcohol deposits cubic crystals during the cooling. Sulphuric acid extracts ammonia from the amminochloride, and gives off arsenic trichloride. L. Pasteur found that ammonia converts the compound into ammonium arsenite. L. Pasteur regarded the product of the action of ammonia on arsenic trichloride as a mixture of ammonia, ammonium chloride, and *arsenic chloroimide*, $2As(NH)Cl+4NH_4Cl+NH_3$. According to C. Hugot, the product of the action of arsenic trichloride and ammonia is always a mixture of ammonium chloride and **arsenic amide,** $As(NH_2)_3$. He also found that between —30° and —40°, ammonia reacts with arsenious chloride, bromide, or iodide, forming arsenic amide together with the corresponding ammonium halide: $AsCl_3+6NH_3=3NH_4Cl+As(NH_2)_3$. Arsenamide is a greyish-white powder, insoluble in liquid ammonia, and stable below 0°, if kept out of contact with moist air; above 0°, it decomposes into **arsenic imide,** $As_2(NH)_3$, and ammonia: $2As(NH_2)_3=3NH_3+As_2(NH)_3$. The decomposition is complete at 60°, and the resulting imide is a stable yellow powder not decomposed in vacuo at 100°, but at 250°, it forms *arsenic nitride*, AsN, and ammonia: $As_2(NH)_3=NH_3+2AsN$, an orange-red powder which, on further heating, decomposes into arsenic and nitrogen. Water decomposes both the amide and the imide into ammonia and arsenic trioxide. According to A. Besson and G. Rosset, when arsenic tetramminotrichloride, prepared at —20°, is treated with liquid ammonia, it loses its colour, and remains colourless when the excess of ammonia is driven off. When extracted with liquid ammonia, ammonium chloride is removed and a white, insoluble residue obtained, the composition of which agrees with that of the imide, $As_2(NH)_3$. Hence liquid ammonia acts chemically on the tetrammine, and not merely as a solvent. Arsenic trichloride also reacts with $AsCl_3,4NH_3$, giving rise to ammonium chloride and a substance or mixture of substances, the composition of which is indicated approximately by the formula $As_4Cl_5N_2H_4$. E. C. Franklin found that when soln. of antimony iodide and potassium amide in liquid ammonia are mixed, an impure *antimony nitride* is formed. A. C. Vournazos[14] prepared a series of **bismuth amines** by direct combination of a tervalent bismuth salt with an inorganic or organic ammonium salt, with salts of primary or secondary amines, either aromatic or aliphatic, and with salts of primary hydrazines. Halides of bismuth yield the most characteristic compounds, but they are also given by the trioxide, nitrate, and phosphate. The bismuthamines are of two kinds, simple, in which the bismuth salt and the amine salt are derived from the same acid and mixed, in which derivatives of different acids unite. As most bismuth salts are easily hydrolyzed, bismuthamines can only be prepared in organic solvents, and from these they separate in crystalline form. The synthesis is best carried out in glacial acetic acid, by adding the bismuth salt as a dry powder or in hot acetic acid soln. to a soln. of salt of the nitrogen compound also in hot acetic acid soln. The product is filtered off. Water or alcohol decomposes the amine; and it is also decomposed by heating it to 400°. *Methylene nitratobismuthate,* $[Bi(NO_3)_4]NH_3(CH)$; and *ammonium iodotrichlorobismuthate,* $NH[BiCl_3I]$, are examples. The compounds do not give the ordinary reactions of bismuth.

F. W. Bergstrom[15] obtained **potassium manganese diamminoamide,** $Mn(NHK)_2.2NH_3$, in light yellow needles, by the action of manganese on a soln. of potassium in liquid ammonia, or better by pouring a soln. of manganese thiocyanate into an excess of a soln. of potassium amide, all in liquid ammonia. The diamminoamide decomposes in vacuo above 100°–120°. By adding potassium amide to a soln. of manganese thiocyanate in liquid ammonia, light yellow **manganese amide,** $Mn(NH_2)_2$, contaminated with some potassium, was formed. It decomposes in vacuo at 140°–175°. According to G. S. Bohart, a soln. of nickel thiocyanate in liquid ammonia gives a precipitate of nickelamide when treated with an eq. amount of potassamide soln. **Nickel amide,** $Ni(NH_2)_2$, is a red, flocculent mass which reacts mildly with water, producing nickel hydroxide and ammonia. When heated at 120° in a vacuum, it yields nickel nitride, Ni_3N_2, a black, amorphous substance which reacts extremely slowly (if at all) with water and dissolves slowly in mineral acids. At 120°, it is decomposed into its constituents. Nickelamide dissolves in an excess of potassamide soln., producing a deep red soln., which deposits a red, crystalline substance, **nickel hexamminopotassamide,** or ammonio-potassium nickelamide, $Ni_2N_3K_5.6NH_3$. It reacts violently with water. Ammonium chromium thiocyanate, $NH_4Cr(SCN)_4.2NH_3$, in liquid ammonia soln., forms at least four different compounds when treated with potassamide. These compounds are, respectively, wine-red, salmon-pink, and purple flocculent precipitates, and a wine-red, crystalline substance. Their composition has not been determined. Potassium nickel cyanide, $2KCN,Ni(CN)_2$, yields three distinct compounds when treated with a soln. of potassamide in liquid ammonia. (1) With excess of the salt, a brownish-red, slightly soluble, crystalline substance is obtained, which has the formula $Ni_3N_2H_2K_4(CN)_6,8NH_3$; when these crystals are kept at ordinary temp. and press., eight mols. of ammonia escape, and a straw-yellow powder, $Ni_3N_2H_2K_4(CN)_6$, remains. (2) With eq. amounts of salt and ammono-base, a lemon-yellow, curdy precipitate is formed; this, when washed with liquid ammonia, crumbles to a heavy powder, having the composition $K(CN)_2Ni.NHK$. (3) With a large excess of potassamide, a deep red soln. is produced, which after twelve hours, deposits deep red crystals of the compound $Ni_3N_{11}H_{22}K_7(CN)_2$.

F. W. Bergstrom[16] obtained **cobaltous amide,** $Co(NH_2)_2$, by the action of cobaltous thiocyanate on potassamide in liquid ammonia. The compound loses ammonia at 120°, forming cobaltous nitride. In 1898, A. Werner and A. Baselli discovered a complex series of cobalt ammines containing an imido-group, the **cobaltic imidoctammines.** G. Vortmann prepared what he called the *fusco-salts* by the oxidation of ammoniacal soln. of cobalt nitrate; and analogous salts were made by S. M. Jörgensen, and E. Frémy. A. Werner and F. Beddow showed that G. Vortmann's salt is really a mixture of dicobaltic oxodiimidoctamminosulphate, and dicobaltic hydrosulphatoimidoctamminosulphate. They prepared G. Vortmann's fuscosulphate as follows:

Cobalt nitrate (150 grams) dissolved in water (50 grams) is mixed with ammonia (500 grams), the soln. gradually heated to boiling and at once filtered; the filtrate is divided into 10 parts, which are placed in flasks and treated with a slow current of air as long as cobalt oxynitrate is precipitated; the dark brown soln. is allowed to remain 12 hours, and then filtered and acidified with dil. sulphuric acid. After a few hours, the precipitate of fusco-sulphate and aquopentammine sulphate is separated by filtration and washed with water until all the aquopentammine sulphate is removed. 200 grams of cobalt nitrate yield 7–7·5 grams of fusco sulphate. The yield, however, varies considerably in each experiment.

A. Werner and A. Baselli, and A. Werner and F. Beddow made **cobaltic imidoctamminotetranitrate,** $Co_2(NH)(NH_3)_8(NO_3)_4.H_2O$; **cobaltic imidoctamminodisulphate.** $Co_2(NH)(NH_3)_8(SO_4)_2.3H_2O$; **cobaltic imidoctamminotetrachloride,** $Co_2(NH)(NH_3)_8Cl_4.5H_2O$; and **cobaltic imidoctamminotetrabromide,** $Co_2(NH)(NH_3)_8Br_4.5H_2O$. They also made dihydrated and hexahydrated **cobaltic oxobisimidobisoctamminooctonitrate,** $O\{Co_2(NH)(NH_3)_8\}_2(NO_3)_8$; **cobaltic oxobisimidobisoctamminotetrasulphate,** $O\{Co_2(NH)(NH_3)_8\}_2(SO_4)_4.6H_2O$; **cobaltic oxobisimidobisoctamminoctochloride,** $O\{Co_2(NH)(NH_3)_8\}_2Cl_8.6H_2O$; and **cobaltic oxobisimidoctamminoctabromide,** $O\{Co_2(NH)(NH_3)_8\}_2Br_3.6H_2O$. They also prepared the series **cobaltic hydronitritoimidoctamminotetranitrate,** $\{Co_2(NH)(NH_3)_8(HNO_2)\}(NO_3)_4.H_2O$; **cobaltic hydronitritoimidoctamminodisulphate,** $\{Co_2(NH)(NH_3)_8(HNO_2)\}(SO_4)_2.H_2O$; and **cobaltic hydronitritoimidoctamminotetrachloride,** $\{Co_2(NH)(NH_3)_8(HNO_2)\}Cl_4.H_2O$. A. Werner, F. Steinitzer, and K. Rücker prepared **cobaltic sulphatoimidoctamminodinitrate,** $\{Co_2(NH)(NH_3)_8(SO_4)\}(NO_3)_2.3H_2O$; and **cobaltic sulphatoimidoctamminodichloride,** $\{Co_2(NH)(NH_3)_8(SO_4)\}Cl_2.3H_2O$. A. Werner and A. Baselli obtained the series **cobaltic hydrosulphatoimidoctamminotrinitrate,** $\{Co_2(NH)(NH_3)_8(HSO_4)\}(NO_3)_3$; **cobaltic hydrosulphatoimidoctamminohydrodisulphate,** $\{Co_2(NH)(NH_3)_8(HSO_4)\}(SO_4)_2H.H_2O$; **cobaltic hydrosulphatoimidoctamminotrichloride,** $\{Co_2(NH)(NH_3)_8(HSO_4)\}Cl_3.2H_2O$; **cobaltic hydrosulphatoimidoctamminodichloronitrate,** $\{Co(NH)(NH_3)_8(HSO_4)\}Cl_2(NO_3)$; **cobaltic hydro-**

sulphatoimidoctamminotribromide, $\{Co_2(NH)(NH_3)_8(HSO_4)\}Br_3.H_2O$; and **cobaltic hydrosulphatoimidoctamminotriiodide**, $\{Co_2(NH)(NH_3)_8(HSO_4)\}I_3$. A. Werner and F. Steinitzer, and A. Werner and A. Mylius prepared a series of salts whose existence had been previously established by F. Rose, and G. Vortmann, and which have been called *melano-salts* : **cobaltic imidohexamminotetranitrate**, $NH\{Co(NH_3)_4(NO_3)_2\}_2.4H_2O$, or $[NH\{CO(NH_3)_3(H_2O)_2\}_2](NO_3)_4$; **cobaltic imidohexamminotetrachloride**, $NH\{Co(NH_3)_3Cl_2\}_2$-HCl ; **cobaltic imidohexamminotetrabromide**, $NH\{Co(NH_3)_3Br_2\}_2$; and **cobaltic imidohexamminotetraiodide**, $NH\{Co(NH_3)_3I_2\}_2$. A. Werner, F. Steinitzer, and K. Rücker prepared **cobaltic ozoimidohexamminotrinitrate**, $[Co_2(O_2)(NH)(NH_3)_6(H_2O)_2](NO_3)_3$ or $Co_2(O_2)(NH)$-$(NH_3)_6(NO_3)_3.2H_2O$; and **cobaltic ozoimidohexamminohydrotrichloride**, $Co_2(O_2)(NH)$-$(NH_3)_6Cl_3.HCl$. A. Werner and F. Steinitzer made **cobaltic hydronitritoimidohexamminotetrachloride**, $\{Co_2(NH)(NH_3)_6(HNO_2)\}Cl_4.H_2O$. A. Werner, F. Steinitzer, and K. Rücker prepared **cobaltic nitratoimidotriaquohexamminotrinitrate**, $[Co_2(NH)(NH_3)_6(H_2O)_3(NO_3)](NO_3)_3$; and **cobaltic nitratoimidotriaquohexamminotrichloride**, $[Co_2(NH)(NH_3)_6(H_2O)_3(NO_3)]Cl_3$. They also prepared the series **cobaltic diozotriimidodecamminonitrate**, $Co_4(O_2)_2(NH)_3$-$(NH_8)_{10}(NO_3)_3.5H_2O$; **cobaltic diozotriimidodecamminoctochloride**, $Co_4(O_2)_2(NH)_3(NH_3)_{10}Cl_8$.$2H_2O$; and **cobaltic diozotriimidodecamminoctobromide**, $Co_4(O_2)_2(NH)_3(NH_3)_{10}Br_8.H_2O$.

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§ 22. Analogies between Liquid Ammonia and Water

In its general chemical and physical properties, ammonia shows a striking resemblance to water.—E. C. FRANKLIN.

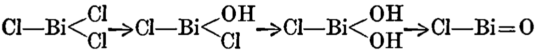
E. C. Franklin and co-workers have emphasized and developed many striking analogies between water and liquid ammonia. Among the well-known solvents, water is characterized by its high boiling point, high specific heat, high heat of vaporization, and fusion, high critical temp. and press., high association factor, and low boiling constant; by its power of uniting with salts as water of crystallization; and, excepting hydrogen cyanide, it is the most powerful ionizing solvent known—and soln. of salts are good conductors of electricity. Ammonia comes next to water in those qualities which give to the latter its unique position among solvents; its boiling point is perhaps low, but it is high in comparison with liquid methane, ethylene, hydrogen sulphide, phosphine, hydrogen chloride, etc. The specific heat of the liquid and the heat of fusion of the solid are greater than those of water; its heat of vaporization, and its critical temp. and press., are high. Ammonia is an associated liquid, and its boiling constant (3·4) is the lowest of any known liquid. It rivals water in its power to unite with salts as ammonia of crystallization; and as a solvent it is scarcely inferior to water, it can readily dissolve some salts which are but slightly affected by water—silver iodide, for instance—and its solvent action on organic compounds exceeds that of water. Ammonia is also an ionizing solvent, indeed, dil. ammonia soln. are even better conductors than dil. aq. soln.

Solvent action.—A great number of organic and inorganic compounds dissolve in ammonia—*e.g.* nitrates, nitrites, cyanides, etc.—*vide supra.* The solubility of the halogen salts in ammonia decreases with increasing at. wt. of the halogen so that the iodides are usually easily soluble, while the bromides and chlorides are but sparingly soluble, and the fluorides almost insoluble; the sulphates, sulphites, and carbonates, phosphates, arsenates, and oxalates, and the hydroxides of the alkalies and alkaline earths are usually sparingly soluble in liquid ammonia, while most are fairly soluble in water. The alkaline earth sulphides and chlorides are precipitated in liquid ammonia. The facility with which ammonia dissolves many organic compounds recalls the properties of alcohol rather than water. Determinations of the lowering of the f.p. and the raising of the b.p. of soln. in ammonia show that compounds have a great tendency to associate or to unite with the solvent.

Chemical reactions in liquid ammonia.—Reactions involving double decomposition takes place in liquid ammonia like they do in water; the reactions are of course modified by the difference in the solubilities of the reacting components in the two solvents so that reactions may take place in the one which do not occur in the other; or the direction of the reaction may be reversed. Thus, sulphides of the alkaline earths separate as white precipitates when soln. of the salts in liquid ammonia are treated with ammonium sulphide; and calcium chloride is precipitated on mixing soln. of sodium chloride and calcium nitrate in liquid ammonia. Reactions between acids and bases are limited by the insolubility of the metallic oxides and hydroxides. Many acids in the form of their ammonium salts dissolve in liquid ammonia and as such exhibit acid properties: (*a*) they discharge the red colour of phenolphthalein produced by the addition of a small quantity of liquid ammonia; (*b*) they dissolve metals like potassium, sodium, calcium, and magnesium with the evolution of hydrogen: $2M+2NH_4X=2MX+2NH_3+H_2$; and (*c*) many oxides and basic salts insoluble in ammonia dissolve in soln. of ammonium salts in liquid ammonia, *e.g.*, sodium and potassium hydroxides, and the oxides of calcium, copper, lead, magnesium, mercury, cadmium, and zinc are soluble in a soln. of ammonium nitrate in liquid ammonia, in a manner analogous to the soln. of the insoluble bases in aq. soln. of the acids: $NaOH+NH_4Cl=NaCl+H_2O+NH_3$; $CaO+2NH_4NO_3=Ca(NO_3)_2+H_2O+2NH_3$. Even in aq. soln. the acid properties of the ammonium salts are sometimes in evidence, witness the soln. of magnesium and mercury hydroxides in soln. of the ammonium salts.

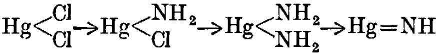
Hydrates and ammoniates.—Judging from records of salts with water of crystallization and also with ammonia of crystallization, ammonia, in its tendency to unite with other compounds, probably exceeds water. Just as a salt may unite with water to form a hydrate, so can salts combine with ammonia to form ammoniates, or ammines, *e.g.* cupric and mercuric chlorides form respectively $CuCl_2.2NH_3$ and $HgCl_2.2NH_3$, etc.

Hydrolysis and ammonolysis.—The hydrolysis of salts has previously been described. Bismuth chloride hydrolyzes in a series of stages which can be symbolized:



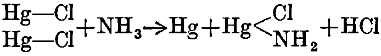
$$\mathrm{Cl{-}Bi}<\!\begin{smallmatrix}\mathrm{Cl}\\ \mathrm{Cl}\end{smallmatrix}\rightarrow\mathrm{Cl{-}Bi}<\!\begin{smallmatrix}\mathrm{OH}\\ \mathrm{Cl}\end{smallmatrix}\rightarrow\mathrm{Cl{-}Bi}<\!\begin{smallmatrix}\mathrm{OH}\\ \mathrm{OH}\end{smallmatrix}\rightarrow\mathrm{Cl{-}Bi{=}O}$$

The corresponding action with liquid ammonia as solvent is termed ammonolysis. *E.g.*:



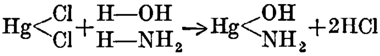
$$\mathrm{Hg}<\!\begin{smallmatrix}\mathrm{Cl}\\ \mathrm{Cl}\end{smallmatrix}\rightarrow\mathrm{Hg}<\!\begin{smallmatrix}\mathrm{NH_2}\\ \mathrm{Cl}\end{smallmatrix}\rightarrow\mathrm{Hg}<\!\begin{smallmatrix}\mathrm{NH_2}\\ \mathrm{NH_2}\end{smallmatrix}\rightarrow\mathrm{Hg{=}NH}$$

When aq. ammonia acts upon mercurous chloride the latter is oxidized to white amidomercuric chloride, $H_2N.HgCl$, and metallic mercury. In symbols:



$$\begin{matrix}\mathrm{Hg{-}Cl}\\ \mathrm{Hg{-}Cl}\end{matrix}+NH_3\rightarrow Hg+\mathrm{Hg}<\!\begin{smallmatrix}\mathrm{Cl}\\ \mathrm{NH_2}\end{smallmatrix}+HCl$$

The jet black colour is produced by the admixture of the finely divided mercury with the white precipitate. With aq. ammonia both hydrolysis and ammonolysis may occur, thus, with mercuric chloride:



$$\mathrm{Hg}<\!\begin{smallmatrix}\mathrm{Cl}\\ \mathrm{Cl}\end{smallmatrix}+\begin{matrix}\mathrm{H{-}OH}\\ \mathrm{H{-}NH_2}\end{matrix}\rightarrow\mathrm{Hg}<\!\begin{smallmatrix}\mathrm{OH}\\ \mathrm{NH_2}\end{smallmatrix}+2HCl$$

The so-called Millon's base, $(HgOH)_2NH_2OH$, is formed as a yellow precipitate when mercuric oxide is boiled with aq. ammonia: $2HgO+NH_4OH\rightleftharpoons(HgOH)_2NH_2OH$; and the precipitate formed when Nessler's reagent reacts with an ammonium salt is to be regarded as an iodide of Millon's base—mercuric ammonohydroxyiodide, that is dimercurihydroxyammonium iodide, $HO-Hg-NH-Hg-I$. The following are typical ammonolytic reactions:

$$SiCl_4+8NH_3\rightleftharpoons Si(NH_2)_4+4NH_4Cl; \qquad 3TeCl_4+16NH_3\rightleftharpoons Te_3N_4+12NH_4Cl$$
$$BCl_3+6NH_3\rightleftharpoons B(NH_2)_3+3NH_4Cl; \qquad PC_3+5NH_3\rightleftharpoons P(NH)NH_2+3NH_4Cl$$

Just as some hydrolytic reactions proceed to completion, others are reversible, so with ammonolytic reactions, some proceed energetically to the end, while others are balanced against a counter-reaction, *e.g.* $HgCl_2+2NH_3\rightleftharpoons NH_2HgCl+NH_4Cl$; and $2HgI_2+4NH_3\rightleftharpoons HgNHgI+3NH_4I$. The following reactions which proceed in aq. soln. resemble the corresponding reactions in liquid ammonia:

$$2AgNO_3+2KOH\rightleftharpoons Ag_2O+2KNO_3+H_2O; \qquad AgNO_3+KNH_2\rightleftharpoons AgNH_2+KNO_3$$
$$HgCl_2+2KOH\rightleftharpoons HgO+2KCl+H_2O; \qquad 3HgI_2+6KNH_2\rightleftharpoons Hg_3N_2+6KI+4NH_3$$
$$2BiCl_3+6KOH\rightleftharpoons Bi_2O_3+6KCl+3H_2O; \qquad BiBr_3+3KNH_2\rightleftharpoons BiN+3KBr+2NH_3$$

Just as with potassium hydroxide in aqueous solutions, sometimes the hydroxide and sometimes the oxide is formed, so in ammonia solutions, potassium amide furnishes the amide, the imide, or the nitride.

Acids, bases, and salts.—To distinguish between the ordinary oxygen salts, acids, and bases and those compounds which bear an analogous relation to ammonia, E. C. Franklin applies the term *hydro-salts*, *hydro-acids*, and *hydro-bases* to those compounds which are related to water, like the *ammono-salts*, *ammono-acids*, and *ammono-bases* are related to the corresponding ammonia derivative. The terms *aquo-salts*, *aquo-acids*, and *aquo-bases* are similarly applied—*e.g.* potassium nitrate is an aquo-salt; potassium hydroxide or calcium is an aquo-base; and acetic acid is an aquo-acid, while potassium acetamide, $CH_3.CO.NHK$, or $CH_3.CO.NK_2$, is an ammono-salt; sodium amide is an ammono-base; and acetamide, $CH_3.CO.NH_2$, is an ammono-acid.

Ammono-acids.—These are represented by the acid amides, acid imides, and acid nitrides. They are soluble in liquid ammonia, and their solutions discharge the colour of alkaline soln. of phenolphthalein; they usually conduct the electric current, and react with the ammono-bases to form ammono-salts. Representatives of the ammono-acids are numerous in organic chemistry, the amides of sulphuric and nitric acids are also well-known, and generally, the amides, imides, and nitrides of the non-metallic elements. Just as the halogen derivatives of the strongly electro-negative elements—*e.g.* arsenic, phosphorus, boron, silicon, etc.—are completely hydrolyzed by water, so the same compounds in liquid ammonia are decomposed, forming compounds which bear analogous relations to the solvent ammonia, as the hydrolytic products bear to water. *E.g.* $AsCl_3+6NH_3\rightleftharpoons As(NH_2)_3+3NH_4Cl$; $SiS_2+4NH_3\rightleftharpoons Si(NH)_2+2NH_4HS$; etc.

Ammono-bases.—This class of compounds is represented by the metal amides, imides, and nitrides,. Just as the hydroxides of the alkali metals are easily soluble in water, so are the amides of the alkali metals readily soluble in liquid ammonia. The solubility of potassamide in liquid ammonia enabled E. C. Franklin to prepare a number of insoluble metal derivatives by bringing together potassamide and the metal salts in ammonia soln. Thus, potassamide reacts with silver nitrate, forming silver amide: $AgNO_3+KNH_2\rightleftharpoons AgNH_2+KNO_3$; with lead nitrate or iodide, lead imide is formed: $Pb(NO_3)_2+2KNH_2\rightleftharpoons PbNH+2KNO_3+NH_3$; and with bismuth iodide, to form bismuth nitride, $BiI_3+3KNH_2=BiN+3KI+2NH_3$. These bases are insoluble in ammonia, but readily dissolve in ammonia solutions of the ammonium salts; and they are decomposed by water with the evolution of ammonia.

Ammono-salts.—The acid and metal amides are related to ammonia much as the ordinary acids and bases are related to water. The acid amides discharge the colour from an alkaline soln. of phenolphthalein in liquid ammonia, while the soluble metal amides give the characteristic colour with the same indicator, and they react with one another in soln. in liquid ammonia, forming metal derivatives of the acid amides in a manner analogous with the interaction of acids and bases in aq. soln., forming a class of compounds related to ammonia as ordinary salts are related to water. The metal and acid amides neutralize one another and phenolphthalein can be used as indicator. Thus, with acetic acid, CH_3COOH, and potassium hydroxide in aq. soln.: $CH_3COOH+KOH\rightleftharpoons CH_3COOK+H_2O$; and acetamide, CH_3CONH_2, and potassamide, KNH_2, in soln. in liquid ammonia, react: $KNH_2+CH_3CONH_2\rightleftharpoons CH_3CONHK+NH_3$. Certain heavy metals amides form ammono-bases and ammono-basic salts by reactions analogous to the formation of insoluble bases and salts from aq. soln. Oxides and hydroxides of some metals are soluble in an excess of a strong base like potassium hydroxide to form a class of salts typified by potassium zincate: $2KOH+Zn\rightarrow Zn(OK)_2+H_2$; and certain metal amides—*e.g.* the amides of nickel, cadmium, silver, aluminium, copper, lead, etc.—are soluble in the amides of more basic elements—*e.g.* potassium amide—to form analogous ammono-salts. For instance, zinc amide or zinc iodide is acted upon by liquid ammonia solution of potassium amide in an analogous manner: $2KNH_2+Zn\rightarrow Zn(NHK)_2+H_2$, and the *potassium ammono-zincate* takes up ammonia of crystallization, forming well-defined crystals. Similarly, the reaction: $SnI_4+4KOH\rightleftharpoons Sn(OH)_4+4KI$ can be contrasted with $SnI_4+4KNH_2\rightleftharpoons Sn(NH_2)_4+4KI$; and the reaction: $Sn(OH)_4+4KOH\rightleftharpoons Sn(OK)_4+4H_2O$, can be contrasted with $Sn(NH_2)_4+4KNH_2\rightleftharpoons Sn(NHK)_4+4NH_3$. The ammonia analogue of potassium stannate is thus *potassium ammono-stannate*, $Sn(NK)_2.4NH_3$, or $Sn(NH_2)_4.2KNH_2$. The following is a selection of examples from E. C. Franklin's list in which the hydro- and ammono-acids bases and salts are compared:

WATER OR OXYGEN TYPE.		AMMONIA OR NITROGEN TYPE.	
I. *Aquo-acids and acid anhydrides.*		*Ammono-acids and acid nitrides.*	
Nitric acid	$NO_2.OH$	Nitramide	$NO_2.NH_2$
Sulphuric acid	$SO_2(OH)_2$	Sulphimide	$SO_2(NH_2)_2$
Carbonic acid	$CO(OH)_2$	Carbamide	$CO(NH_2)_2$
Orthosilicic acid	$Si(OH)_4$	Silicon amide	$Si(NH)_2$
Silicic anhydride	SiO_2	Silicon nitride	Si_3N_4
II. *Aquo-bases and basic oxides.*		*Ammono-bases and basic nitrides.*	
Lithium hydroxide	$LiOH$	Lithium amide	$LiNH_2$
Lithium oxide	Li_2O	Lithium nitride	Li_3N
Calcium hydroxide	$Ca(OH)_2$	Calcium amide	$Ca(NH_2)_3$
Mercuric oxide	HgO	Mercuric nitride	Hg_3N_2
Bismuth oxide	Bi_2O_3	Bismuth nitride	BiN
III. *Aquo-salts.*		*Ammono-salts.*	
Potassium sulphate	$SO_2(OK)_2$	Dipotassium sulphamide	$SO_2(NHK)_2$
Potassium acid sulphate	$SO_2.OH.OK$	Monopotassium sulphamide	$SO_2(NH_2)NHK$
Potassium carbonate	$CO(OK)_2$	Dipotassium urea	$CO(NHK)_2$
Potassium acid carbonate	$CO.OH.OK$	Monopotassium urea	$CO(NH_2)NHK$
Potassium acetate	$CH_3.COOK$	Potassium acetamide	$CH_3.CO.NK_2$
IV. *Amphoteric hydroxides, etc.*		*Amphoteric amides, imides, and nitrides.*	
Zinc hydroxide	$Zn(OH)_2$	Zinc amide	$Zn(NH_2)_2$
Silver hydroxide (?)	$AgOH$	Silver amide	$AgNH_2$
Lead hydroxide	$Pb(OH)_2$	Lead imide	$PbNH$
Thallium hydroxide (?)	$TlOH$	Thallium nitride	Tl_3N
Potassium stannate	$K_2SnO_3.3H_2O$	Potassium ammonostannate	$K_2Sn(NH)_3.3NH_3$
V. *Aquo-basic salts.*		*Ammono-basic salts.*	
Basic mercuric chloride	$xHgCl_2yH_2O$	Basic mercuric chloride	$NH_2HgCl.HgCl_2$
Basic lead iodide	$xPbI_2yPbO$	Basic lead iodide	$PbNI.2NH_3$

Ionization of liquid ammonia and water solutions.—Solutions of certain salts in liquid ammonia are good conductors of electricity so that liquid ammonia approaches water in its ionizing power. The effect, however, is largely due to the high speed at which the ions are supposed to travel in the solvent. For example, E. C. Franklin and H. P. Cady [1] find that univalent ions travel, at −33°, nearly three times as fast as in aq. soln. at 18°. Just as the solvent water, in the ionization theory of hydrolysis, is supposed to be ionized $H_2O=OH'+H^{\cdot}$, so in ammonolysis, the solvent ammonia is supposed to be ionized $NH_3=NH_2+H^{\cdot}$. Sodamide, $NaNH_2$, furnishes sodium ions $Na^{\cdot}$ and amide ions NH'_2 when dissolved in liquid ammonia, and it is to be considered as a base. It reddens phenolphthalein. The neutralization of this solution results in the union of $H^{\cdot}$ ions with NH_2 ions to form ammonia molecules, just as the neutralization of bases is regarded as an effect of the union of $H^{\cdot}$ and OH' ions. Acetamide, $CH_3.CO.NH_2$, ionizes in liquid ammonia in an analogous manner: $CH_3.CO.NH_2 \rightleftharpoons CH_3.CO.NH'+H^{\cdot}$, and it thus behaves as an acid.

REFERENCES.

[1] E. C. Franklin and C. A. Kraus, *Amer. Chem. Journ.*, **20**. 820, 1898; **21**. 1, 8, 1899; E. C. Franklin, *ib.*, **21**. 8, 1899; **23**. 277, 1901; **28**. 83, 1906; *Journ. Amer. Chem. Soc.*, **27**. 191, 821, 1905; E. C. Franklin and H. P. Cady, *ib.*, **26**. 499, 1904; F. W. Bergstrom, *Journ. Phys. Chem.*, **29**. 160, 1925.

§ 23. Hydroxylamine

Ammonia is the end-product of the reduction of nitric oxide by hydrogen: $2NO+5H_2 \rightarrow 2H_2O+2NH_3$; the reduction, however, may take place in stages: $NO \rightarrow NH_2OH \rightarrow NH_3$. When the conditions are favourable, the incompletely reduced intermediate compound may predominate among the products of the reduction. The compound, symbolized NH_2OH, is called **hydroxylamine,** because it can be regarded as water with a hydrogen atom replaced by the amine-group, NH_2. E. Wagner compared hydroxylamine with hydrogen dioxide, where one HO-group is replaced by a NH_2-group. Hydrogen dioxide is obtained by reducing oxygen; hydroxylamine, by reducing oxygen derivatives of nitrogen. Both compounds are unstable, one producing water and oxygen, the other ammonia and oxidation products. From the opposite point of view, hydroxylamine, together with *dihydroxyammonia*, $NH(OH)_2$, can be regarded as intermediate compounds in the oxidation of ammonia:

NH_3	NH_2OH	$NH(OH)_2$	$N(OH)_3$
Ammonia.	Hydroxylamine.	Dihydroxyammonia.	Orthonitrous acid.

E. Divers and T. Shimidzu believed that in the reduction of dil. nitric acid by zinc, ammonia and hydroxylamine are not consecutive products, but are produced by parallel and independent reactions. They said that when once formed, hydroxylamine is not readily reduced to ammonia, and is therefore not necessarily an intermediate stage in the reduction to ammonia. They also showed that the presence of sulphuric acid favours the formation of hydroxylamine, but no explanation of this peculiar effect has yet been made. By using a great excess of sulphuric acid they found, in accord with J. B. Kinnear's result, that nearly, if not all the nitric acid unconverted to hydroxylamine is converted into ammonia. N. R. Dhar suggested that ammonia being more basic than hydroxylamine is more difficult to form in strongly acidic soln. In opposition to O. von Dumreicher, E. Divers and T. Haga said that an acidified soln. of stannous chloride does not reduce nitric oxide to ammonia if no air (nitrogen peroxide) be present. Under these circumstances only hydroxylamine is produced. The reduction does not occur at 100°, the reduction is small at 90°, and as the temp. falls, the reaction becomes more and more pronounced. One of the old terms for hydroxylamine is *oxyammonia.* The second oxidation product, $NH(OH)_2$, has not been isolated; but in a paper *Ueber das Hydroxylamine*, 1865, W. Lossen[1] announced the discovery of hydroxylamine among the reduction products of nitric acid or nitric oxide by nascent hydrogen: $2NO+3H_2 \rightarrow 2NH_2OH$. W. Lossen's discovery of hydroxylamine not only threw much light on the nature of the reduction of nitric acid, but it also enriched chemistry with a substance which possessed interesting and useful properties. Hydroxylamine has proved of great value in studying the structure of organic compounds; it has been used in photography; as an antiseptic; as a reducing agent in analytical and synthetic chemistry; etc.

The preparation of hydroxylamine salts.—Hydroxylamine is formed by the reducing action of nascent hydrogen on nitric oxide, nitric acid, nitrous acid, certain nitrates, or nitro-bodies. For instance, W. Lossen passed a stream of nitric oxide through a soln. of tin dissolving in hydrochloric acid: $2NO+3H_2=2NH_3O$. The soln. will contain a compound of hydroxylamine and hydrogen chloride—hydroxylamine hydrochloride—and also tin chloride. The tin may be precipitated by passing hydrogen sulphide through the soln. The liquid is then filtered and evaporated to dryness. The residue is extracted with absolute alcohol, and, on evaporation, white crystals of hydroxylamine hydrochloride, $NH_2OH.HCl$, are obtained. E. Ludwig and T. Hein, and E. Divers and T. Haga, and E. Divers and T. Shimidzu used a similar process. E. Frémy reduced nitrous acid and nitrates by tin and hot conc. hydrochloric acid; E. J. Maumené, ammonium nitrate; J. Donath, sodium nitrate; and B. Lengyel, potassium nitrate. W. Lossen obtained hydroxylamine by the action of tin on nitric acid, and E. Divers showed that the presence of hydrochloric or sulphuric acid favours the reaction. L. H. Milligan and G. R. Gillette studied the reduction of free nitric acid by stannous chloride, ferrous salts, and by titanous salts—*vide infra*, nitric acid. W. Lossen, and B. Lengyel obtained the base by the action of tin and hydrochloric acid on ammonium, potassium, sodium, or ethyl nitrate ; E. Frémy, and E. Divers and T. Haga, by the action of hydrogen sulphide, sulphur dioxide, and sulphides on nitric acid ; E. Divers and T. Haga, by treating silver nitrite suspended in water, or a mixture of copper sulphate and potassium nitrite with hydrogen sulphide ; or by treating silver or mercurous nitrite with sulphurous acid ; E. Divers and T. Haga, and F. Raschig, by reducing sodium nitrite with sulphites ; A. Lidoff, by reducing nitrites, say mercury or silver nitrate, with hyposulphurous acid ; E. Divers, E. Frémy, and E. J. Maumené, by reducing, say, sodium nitrite with sodium amalgam ; and A. Jouve, by reducing nitric acid with hydrogen in the presence of spongy platinum between 115° and 120°. M. Coblens and J. K. Bernstein observed that hydroxylamine is formed when silver hyponitrite or a soln. of sodium nitrite is added drop by drop to an acid soln. of stannous chloride.

C. F. Böhringer, and J. Tafel recommended making hydroxylamine by the electrolytic reduction of nitric or nitrous acid, or the corresponding salts, in a partitioned cell containing sulphuric acid with nitric acid in the cathode compartment, and amalgamated lead electrodes. E. P. Schoch and R. H. Pritchett used as anode a lead pipe or rod about 1 inch in diameter instead of a graphite rod. The cathode compartment is filled with a mixture of three vol. water to one vol. of hydrochloric acid (sp. gr. 1·20). The anode liquid is cooled by causing it to circulate continually through a lead pipe coil immersed in the freezing mixtures used to cool the cathode liquid. The current used is 50 ampères at 25 volts, and the nitric acid (sp. gr. 1·4) mixed with one vol. of water is run into the cathode compartment at the rate of 30 c.c. per hour, the addition being allowed to proceed for two and a half hours. The cathode liquid is concentrated in vacuo on a water-bath, and the hydroxylamine chloride freed from ammonium chloride by crystallization from alcohol. G. Ponzio and A. Pichetto recommended the following method of preparation :

A convenient cell consists of a glass beaker, 8·5 cms. wide and 15 cms. high, the anode being a cylinder 4·7 cms. in internal diameter and about 110 sq. cms. in area, made of lead sheet 1·2 mm. thick, and the cathode a similar cylinder, 7 cms. in diameter, about 100 sq. cms. in area, and with 30 holes 0·5 cm. in diameter. An ordinary porous pot, 5·5 cms. wide inside and 3·5 mm. thick, served as diaphragm, and the anolyte is composed of 200 c.c. of sulphuric acid having a sp. gr. of 1·553 at 15°, and the catholyte of 150 c.c. of the same acid containing in soln. 10 g. of sodium nitrate. A current of 5 amps. is maintained by means of a potential difference of 3·7–3·6 volts between the electrodes, and the cell is kept immersed in cold water during the electrolysis. When the nitrate ions completely disappear, this occupying 2–3 hrs., further quantities of 10 g. of sodium nitrate are added, a total amount of 60 g. being employed. The current efficiency amounts to 20–22 per cent., and the yield of hydroxylamine calculated on the sodium nitrate, to 14·5–15 per cent. of the theoretical. To isolate the hydroxylamine, the neutralized cathodic liquid is heated to 70°–80° with acetone, and after 12 hrs., the separated sodium sulphate crystals are filtered off and washed with benzene, with which also the filtrate is extracted four times. The benzene soln. is shaken with 20 per cent. hydrochloric acid, the acid soln. being conc. to small volume by boiling and then evaporated to dryness on a water-bath. The hydroxylamine hydrochloride thus obtained is quite free from ammonium salts and becomes perfectly white if crystallized once from one-half its weight of water.

J. Tafel electrolyzed a soln. of 0·4 grm. of nitric acid and 20 c.c. of 50 per cent. sulphuric acid, using 10 sq. cms. of cathode surface and 2·4 amps. at 0°. The product of the reduction is largely dependent on the nature of the metal used as electrode. Some results are indicated in Table XXVII. With platinum, no ammonia or hydroxylamine was formed, and with palladium the reduction is extremely slow. The chief products of the reduction are hydroxylamine and ammonia. The largest proportion of the hydroxylamine is formed when mercury is used as cathode, and the conversion of the nitric acid into this can be carried out almost quantitatively. With lead electrodes, about 40 per cent. of the nitric acid is converted into hydroxylamine, and with copper electrodes only about 15 per cent. ; if the copper be in the form of a spongy mass, only about one per cent. of the acid is transformed into hydroxylamine, the remainder being reduced to ammonia. When an amalgamated (lead, tin, or copper) cathode is used, the reduction takes place in the same way as when a mercury cathode is employed. Hydroxylamine is not reduced when subjected to electrolysis between copper electrodes ; and the reduction of nitric acid does not, at least between copper electrodes, always go through the hydroxylamine stage.

TABLE XXVII.—THE ELECTROLYTIC REDUCTION OF NITRIC ACID.

Cathode material.	Nature of surface.	Time hrs.	Products of reduction.			
			NH_2OH	NH_3	HNO_2	Gas.
Lead . .	prepared	2·5	24·7	59·9	0·8	7·3
Lead . .	amalgamated	2·5	69·7	16·9	0·1	9·2
Tin . .	polished	3·0	43·3	40·4	0·7	7·3
Copper . .	polished	2·5	11·5	76·8	trace	7·1
Copper . .	spongy	2·5	1·3	93·0	0·1	3·4
Silver . .	polished	3·0	22·3	47·2	1·5	19·7

The amount of hydroxylamine produced is greater as the soln. of nitric acid is more dil. ; in order to obtain the largest proportion, a very dil. soln. of nitric acid should be used, and more added as the reduction proceeds. When the amount of sulphuric acid present falls below 40 per cent., the quantity of hydroxylamine formed decreases appreciably, but otherwise the conc. of the sulphuric acid exerts no influence on the reaction. In the production of hydroxylamine, the current yield is greatest for lead, slightly less for amalgamated lead, and decidedly less for copper. The presence of nitrous acid is said to exert no appreciable influence on the reduction of nitric acid at cathodes of these metals. E. Divers, and J. Tafel agree that the yield of hydroxylamine increases with increasing conc. of sulphuric or hydrochloric acid, although E. Divers observed that with the latter, the yield passes through a maximum. H. E. Patten made some observations on this subject. The relation of sulphuric acid to the yield of hydroxylamine is not known. E. Divers said that there is no reason to believe that the action of the hydrochloric or sulphuric acid upon the metal is instrumental in forming hydroxylamine. The second acid serves to decompose the metal nitrate as fast as it is produced. In this way, it holds the hydroxylamine in a state more stable than the nitrate. This agrees with the observations of O. Flaschner, that hydroxylamine lowers only slightly the decomposition voltage of $2N$-H_2SO_4 at a mercury cathode, while that of $2N$-HNO_3 is lowered nearly 0·4 volt. This means that under the given conditions nitric acid is a better oxidizing agent than hydroxylamine and will be used up before the hydroxylamine : E. J. Joss also found nitrous acid is slightly less powerful than nitric acid. E. Divers's second point, (ii) that the second acid preserves the hydroxylamine from the destructive action of the nitrous acid, by preventing the formation of this substance which would otherwise result from the reaction between the metal yielding hydroxylamine and its own nitrate. J. Tafel, however, found that this is not correct because nitrous acid has very little effect on the reduction. E. Divers's third point, (iii) that the second acid determines the reduction of all the nitric acid to hydroxylamine by supplying the hydrogen for reducing it, and so keeping it free to the last. J. Tafel, however, doubted this because in very conc. soln., the free acid or $H^{\cdot}$-ion conc. is low.

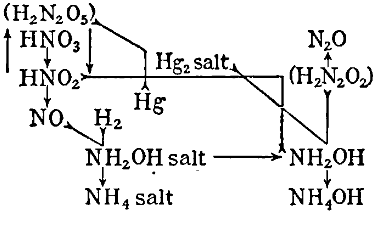
J. Tafel further showed that the production of ammonia does not always pass through the hydroxylamine stage. He said :

> Nitric acid dissolved in sulphuric acid is reduced electrolytically at an amalgamated cathode almost exclusively to hydroxylamine, although such a cathode has a distinct electrolytic reducing action on hydroxylamine sulphate. On the other hand, nitric acid is reduced almost completely to ammonia at a copper cathode which is effective only at

> low current densities and which is quite inadequate to reduce hydroxylamine sulphate any further. The only safe conclusion to draw is that the electrolytic reduction of nitric acid to ammonia at a copper cathode does not pass through the hydroxylamine stage. Certain cathode materials, such as copper, for instance, by a chemical action divert the reduction process somewhere between nitric acid and hydroxylamine from the sp. electrolytic course so that the reaction goes direct to ammonia, without passing through the hydroxylamine stage. I cannot tell certainly at what stage the switching of the reaction takes place ; but it seems not improbable that it occurs at dihydroxylamine, $NH(OH)_2$.

J. Tafel could not reduce hydroxylamine at the copper cathode, but it passes to ammonia at the amalgamated copper cathode. O. Flaschner, however, did reduce the hydroxylamine at the copper cathode, because, added J. Tafel and H. Hahl, he worked with soln. so dil. that the hydrolyzed hydroxylamine undergoes reduction, not the hydroxylamine itself. The hydrogen over-voltage at the amalgamated copper cathode is higher than it is at a copper cathode, and hence reducing effects may be possible with the former and not possible with the latter. All the amalgamated cathodes used by J. Tafel gave high yields of hydroxylamine ; this is taken to be a specific property of the mercury since no mercury ions are present. The high over-voltage of mercury might be expected to carry the reduction to the ammonia stage. He found that no hydroxylamine is produced when mercury is treated with nitric acid. It was accordingly inferred that the chemical and electrolytic processes are different. J. A. Wilkinson showed that the different results are determined by the presence of mercury ions ; if the conc. of the mercury ions be kept low, the chemical process also furnishes hydroxylamine. J. Tafel's experiments show that hydroxylamine does not depolarize the decomposition of 50 per cent. sulphuric acid at a copper cathode. E. Müller showed that there is a peculiar relation between the conc. of the acid and the depolarizing power of hydroxylamine because the oxidizing power of hydroxylamine in alkaline soln. is greater than that of either the nitrate or the nitrite ; and no appreciable yield of hydroxylamine could be obtained by the electrolysis of neutral soln.

V. Sihvonen studied the electrolysis of nitric acid with platinum or copper cathodes, with a cathode of mercury in phosphoric or sulphuric acid at 25°–40° ; and also the electrolysis of hydroxylamine with the same cathodes. His idea of the mechanism of the reactions in the two cases is illustrated by :



where the symbols of the hypothetical intermediate compounds are bracketed. The compounds following one another in the scheme are reduced in acidic soln. with increasing cathodic potential. Down to nitric oxide, the reduction proceeds without the evolution of hydrogen—*vide infra*, nitric acid.

According to E. Carstanjen and A. Ehrenberg, and A. Steiner, hydroxylamine hydrochloride is formed when mercury fulminate, $C_2N_2O_2Hg$, is treated with hydrochloric acid ; R. Preibisch obtained it by the reduction of aliphatic nitro-compounds—*e.g.* nitro-methane ; V. Meyer and J. Locher, and G. Chancel, by reducing dinitropropane, dinitrobutane, ethylnitrolic acid, and the ammonium salt of nitroform ; and J. Kachler, by reducing dinitroheptylic acid. In E. Divers and T. Haga's process hydroxylamine disulphonate, $N(HSO_3)OH$, is first prepared by the interaction of sodium nitrite and sodium sulphide, and this is subsequently decomposed by heating it with water, whereby hydroxylamine sulphate is produced. Details are as follow :

Conc. soln. of two mol. eq. of sodium nitrite and one of sodium carbonate are treated with sulphur dioxide until the mixture has an acid reaction. The sodium salt of hydroxylamine disulphuric acid, $HO.N(HSO_3)_2$, is formed, and this decomposes on the addition of a little sulphuric acid into the sodium salt of hydroxylamidosulphonic acid, $HO{\cdot}NH.HSO_3$, and sodium hydrosulphate, $NaHSO_4$. When the first-named salt has stood a couple of days at 90°–95°, it breaks down still further into hydroxylamine, $HO{\cdot}NH_2$, and sodium bisulphate. The latter is first crystallized from the soln., and crystals of hydroxylamine sulphate are subsequently separated. Potassium salts do not give so good a yield as the sodium salts. Very little ammonia is formed. W. L. Semon modified this process.

The isolation of hydroxylamine.—W. Lossen prepared an aq. soln. of the free base (i) by adding the proper amount of baryta-water to precipitate all the combined sulphuric acid as barium sulphate; and (ii) by treating a conc. aq. soln. of the sulphate or nitrate with an alcoholic soln. of potassium hydroxide, whereby potassium sulphate or nitrate is precipitated. When the attempt is made to concentrate the aq. soln. of the base by evaporation in vacuo, the soln. begins to decompose; and if the aq. soln. is distilled, a great proportion of the hydroxylamine is decomposed into ammonia, etc., and the remainder passes along with steam to the receiver.

Up to 1890, hydroxylamine was known only in the form of its salts or in aq. soln. W. Lossen tried, without success, to isolate the base by distilling the aq. soln. C. A. Lobry de Bruyn assumed that the presence of water was the secret of W. Lossen's failure to isolate the base, and he tried alcohol as solvent. Solubility of the hydroxylamine in methyl alcohol was found to be greater than in ethyl alcohol. He succeeded in isolating the base by distillation from a mixture of sodium methoxide, and hydroxylamine chloride.

To isolate hydroxylamine, dissolve the hydrochloride in methyl alcohol and add sodium methylate (obtained by dissolving metallic sodium in methyl alcohol). Filter off the sodium chloride, and remove the alcohol by distillation—at first under ordinary press. and then under reduced press. The hydroxylamine distils at about 70° under a press. of 60 mm.; or at, say, 58° under a press. of 22 mm. The method was modified a little by J. Houben, H. Lecher and J. Hofmann. A 40 per cent. yield was obtained by using absolute alcohol; and C. D. Hurd and H. J. Brownstein, obtained a 50 per cent. yield by using butyl alcohol. The explosive properties of the hydroxylamine and the precautions to be taken in its preparation were discussed by C. A. Lobry de Bruyn, J. W. Brühl, R. Uhlenhuth, and R. Wolffenstein and F. Groll. Almost at the same time as C. A. Lobry de Bruyn, L. Crismer obtained the base by passing ammonia through a mixture of ether with the complex salt zinc hydroxylamine chloride, $ZnCl_2{\cdot}2NH_2OH$; he distilled off the ether, and finally the hydroxylamine. R. Uhlenhuth isolated the base by distillation from the phosphate under diminished press. According to E. Ebler and E. Schott, the solid can be further purified by crystallization from alcohol at —18°, when conc. soln. deposit the base in white leaflets, and dil. soln. in needles. O. Baudisch and F. Jenner added finely powdered and dried hydroxylamine sulphate to liquid ammonia in a quartz tube, and removed the ammonia by evacuation; the free hydroxylamine was extracted by alcohol.

The physical properties of hydroxylamine.—Anhydrous hydroxylamine furnishes transparent plates (L. Crismer), needles (C. A. Lobry de Bruyn, and J. W. Brühl), without taste or smell. H. Lecher and J. Hofmann said that the crystals obtained from ethyl alcohol, or by the solidification of the molten substance, are identical, and belong to the rhombic system. C. A. Lobry de Bruyn gave 1·35 for the sp. gr. of the crystals at 18°; and 7·235 for the molten salt. J. W. Brühl gave 1·2255 for the sp. gr. at 0°/4°; 1·2156 at 10°/4°; and 1·2044 for the liquid at 23·5°/4°. E. Schott obtained very different values for the highly purified hydroxylamine; he gave 1·0742 at 19·1°/4°; and 1·0717 for 20°/4°. H. Lecher and J. Hofmann gave 1·335 at 10°, and 1·334 at 14°. Considering hydroxylamine as the amido-derivative of water, C. A. Lobry de Bruyn inferred that hydroxylamine would be solid at ordinary temp. because the substitution of a NH_2-group in place of hydrogen usually raises the b.p. and the m.p. The argument from analogy turned out to be correct. The crystals when first prepared melt at 33°, and after standing for some hours, they melt at 27·5°. J. W. Brühl gave 32°–33° for the freezing temp., and in a capillary tube, they fused at 33°–34°. H. Lecher and J. Hofmann gave 32°–35° for the m.p. According to C. A. Lobry de Bruyn, if the cooling liquid be at rest, it can be under-cooled down to 0°—solidification occurs instantly if the liquid be then shaken. The b.p. is 56°–57° under 22 mm. press. At ordinary press., hydroxylamine gradually decomposes if kept over 15°, and at higher temp. it is liable to explode with a yellow flash. H. Lecher and J Hofmann's preparation was less stable than that of C. A. Lobry de Bruyn, for it smelt of ammonia after keeping 24 hrs., and in 4 days it completely liquefied and contained only 42·55 per cent. of hydroxylamine. C. A. Lobry de Bruyn said that if hydroxylamine be heated slowly on platinum foil, it burns with a yellow flame ; but if a drop be heated in a test-tube over the free flame, it explodes with a loud noise. The solid decomposes on standing a short time in air. G. M. J. MacKay found the mol. depression of the f.p. to be 1·77°, 1·90° and 2·25° respectively for soln. with a mol of hydroxylamine in 1, 20, and 500 litres of soln. These results agree with the conductivity measurements in showing a slight ionization of the hydroxylamine in aq. soln. M. Berthelot and C. Matignon gave —3·8 Cals. per mol for the heat of soln. in water ; and M. Berthelot and G. André, 23·8 Cals. for the heat of formation in aq. soln.

W. N. Hartley and J. J. Dobbie examined the spectrum of hydroxylamine ; and W. B. Brodie, the spectrum of blood treated with hydroxylamine. C. A. Lobry de Bruyn reported the index of refraction at 14° to be $\mu_\alpha=1{\cdot}44123$; $\mu_\beta 1{\cdot}45025$; and $\mu_A=1{\cdot}43035$; and at 40°, $\mu_\alpha=1{\cdot}43350$; $\mu_\beta=1{\cdot}44299$; and $\mu_A=1{\cdot}42298$. J. W. Brühl gave at 23·5°, 1·43754 for the Li-ray ; 1·44323 for the Tl-ray ; 1·43801 for the H_α-ray ; 1·44652 for the H_β-ray ; 1·44047 for the Na-ray ; and 1·45137 for the H_γ-ray. This makes for the dispersion $\gamma-\alpha=0{\cdot}0057$, or $M(\gamma-\alpha)=9{\cdot}19$. E. Schott gave at 14·5°, $\mu=1{\cdot}41723$ for the H_α-line ; 1·41952 for the Na-line ; 1·42476 for the H_β-line ; and 1·42917 for the H_γ-line, giving $M(\gamma-\alpha)=8{\cdot}09$. According to E. Schott, the mol. refraction for NH_2OH is 7·257 and the dispersion 0·211 ; and for $H_3N=0$, 8·14, and 0·59.

E. C. Szarvasky found that the electrolysis of hydroxylamine was accompanied by the spontaneous transformation of hydroxylamine into ammonia. Secondary reactions always occur—the base being reduced to ammonia at the cathode and at the anode oxidized to nitrogen oxides. F. Balla found that with various electrodes the percentage current yield of $NaNO_2 : NaNO_3$ in the electrolytic oxidation of hydroxylamine with anodes of different metals was as follows :

	Pt	Cu	Fe	N	Co	Pb	C	Graphite
$NaNO_2$.	35·10	33·51	41·13	44·49	45·44	21·66	8·06	31·18
$NaNO_3$.	17·09	16·06	1·53	5·53	9·74	32·10	35·59	32·49

Thus, copper and platinum give similar results ; the nitrite formation is greater with iron, nickel, and cobalt, and the nitrate formation less. The gases were mainly nitrous oxide and nitrogen with a small proportion of oxygen. N. D. Zelinsky and S. G. Krapiwin showed that the decomposition of hydroxylamine into acid and base does not occur in soln. with methyl alcohol as solvent. J. Tafel showed that an aq. soln. of hydroxylamine sulphate in presence of 20–50 per cent. of sulphuric acid is not reduced at a copper cathode. O. Flaschner observed some reduction in dil. sulphuric acid soln. J. Tafel and H. Hahl found that reduction always takes place when the sulphuric acid conc. in the layer of electrolyte in contact with the cathode is reduced beyond a certain point, and when there is no excess of acid ; in other words, when hydroxylamine sulphate itself is electrolyzed, the reduction is quantitative. These results are most readily accounted for on the view that only free hydroxylamine (produced in this case by partial hydrolysis of the sulphate), but not the hydroxylammonium ion, $NH_3OH^{\cdot}$, is reduced at a copper cathode. The subject was discussed by H. E. Patten, V. Rothmund and O. Flaschner, and J. Tafel—*vide supra.*

The electrical conductivity was measured by W. H. Ross, who found that in all cases the conductivity of the salt soln. was increased with time, especially with the more dil. soln. This is due to the decomposition of the salts under the influence of the platinum-black of the electrodes; with polished electrodes, the effect is considerably smaller. The base itself is oxidized even more rapidly than the salts. The soln. are in all cases decomposed by the platinum electrodes, and G. M. J. MacKay showed that tin does not decompose the soln. at all, while copper decomposes the soln. completely. The order in which the metals were found to decompose the soln. is: tin, platinum, silver, nickel, mercury, and copper. The electrical conductivity of hydroxylamine, using tin electrodes, in terms of mercury at 18°, with v vols. of soln. per mol, is as follows:

v	0·0994	0·5	1·0	5·0	10	20	50	100	200	500
μ	0·031	0·02	0·051	0·098	0·28	0·40	0·52	0·76	1·3	1·4

There is therefore a minimum mol. conductivity between the $2N$- and $10N$-conc., which may indicate that at high concs., hydrates are formed which are dissociated on further dilution, but this point was not further investigated. The sp. conductivity in reciprocal ohms of pure hydroxylamine at a temp. slightly above 33° was found to be approximately 83×10^{-6}, a value which lies between that of liquid ammonia at 30°, 150×10^{-6}, and that of hydrazine hydrate, 34×10^{-6}. W. A. Noyes and J. H. Hibben made some transport experiments with some ionizable derivatives of hydroxylamine. K. Winkelblech found 2·5 per cent. hydrolysis in aq. soln. of hydroxylamine hydrochloride at 25° with soln. containing a mol of the salt in 1024 litres of water; and V. H. Veley, 8·1 per cent. at 15° with a mol of salt in 10,000 litres. E. O. Ellingson obtained results about 0·3 to 2·6 per cent. higher than J. Thomsen for the heats of neutralization of hydroxylamine with acids. E. O. Ellingson found for hydroxylamine and hydrochloric acid, concentration 1 : 50, 9483 cals., and conc. 1 : 200, 9292 cals.; for hydroxylamine and sulphuric acid, conc. 1 : 50, 11,445 cals., and conc. 1 : 200, 11,071 cals.; for hydroxylamine and trichloracetic acid, conc. 1 : 100, 9681 cals.; and conc. 1 : 200, 9280 cals.

The chemical properties of hydroxylamine.—According to C. A. Lobry de Bruyn, free hydroxylamine may produce a blister if a drop rests on the skin for a short time, but no ill-effects were noticed from the vapours when working with this substance. G. Bertoni and C. Raimondi observed that intravenous or subcutaneous injections have a poisonous action, and nitrous acid can then be detected in the blood. A. Pasquali said that the salts of hydroxylamine are poisonous, but large doses are needed to produce fatal effects; he found the lethal dose for dogs to be 0·032 grm. per kgrm. of body weight. R. Cuisa and R. Luzzatto say that hydroxylamine is four to five times as powerful a poison as nitrous acid. T. L. Brunton and T. J. Bokenham found that hydroxylamine reduces the blood press. like amyl nitrite. L. Lewin, C. Binz, and G. Bertoni and C. Raimondi noted the changes produced in blood corpuscles by hydroxylamine. W. Lossen said that the alcoholic soln. irritates and reddens the skin. The toxic action of hydroxylamine on bacteria, and infusoria was observed by G. Bertoni, W. Gibbs and E. J. Reichert, P. J. Eichkoff, O. Löw, G. Marpmann, W. B. Brodie, and A. Pasquali; M. Raciborsky, however, showed that hydroxylamine is assimilated by some fungi. V. Meyer and E. Schulze found that hydroxylamine salts retard the development of plants or else kill them.

C. A. Lobry de Bruyn said that if hydroxylamine be of a high degree of purity, it may be kept for months without decomposition; its decomposition is favoured by alkalies, so that the glass vessels in which it is to be kept must be well washed with acids. A number of salts also favour the decomposition of hydroxylamine. According to J. W. Brühl, the solid is stable at low temp., and molten under-cooled hydroxylamine, at 0°, does not decompose. Decomposition commences at about 10° with the formation of small bubbles of gas—mostly nitrogen; the decomposition at about 20° proceeds steadily, and this the faster, the higher the temp. C. A. Lobry de Bruyn said that nitrogen and nitrous oxide are formed by the spontaneous decomposition of hydroxylamine or ammonium nitrite. According to K. A. Hofmann and F. Kroll, the slow decomposition of hydroxylamine hydrochloride at about 150°, takes place in accordance with the equations: $3NH_2.OH=N_2+NH_3+3H_2O$ and $4NH_2.OH=N_2O+2NH_3+3H_2O$. The addition of basic substances represses the second in favour of the first change to an extent which is less than would be expected, whereas acidic substances displace the action in the contrary direction. Nitrous acid or nitrite is produced by the acid or alkaline fusion of hydroxylamine. It is therefore probable that hydroxyhydrazine is produced initially from 2 mols. of hydroxylamine and subsequently converted into the diamide of nitrous acid, $OH.N(NH_2)_2$; this is hydrolyzed to ammonia and nitrous acid (or nitrosyl acid in conc. acid soln.) which, with unchanged hydroxylamine, yields nitrous oxide. Confirmation of this hypothesis is found in the observation that nitrous oxide is not formed in the presence of sufficient alkali or of carbamide. In alkaline soln. the diamide of nitrous acid suffers mainly intramolecular decomposition, $OH.N(NH_2)_2=N_2+NH_3+H_2O$, accompanied by the subsidiary change: $OH.N(NH_2)_2+NaOH=NaNO_2+2NH_3$. A. Kurtenacker and F. Werner found that the course of the decomposition of hydroxylamine in alkaline soln. depends on the conc. of the alkali, on the temp., and on the nature of any catalyst present. The higher the alkali conc.—in the absence of a catalyst or in the presence of pumice, platinized pumice, or platinum gauze—the smaller the proportion of nitrous oxide and the greater the proportion of nitrogen formed. In the presence of platinum-black, the proportion of nitrous oxide formed increases slightly with a rise in the conc. of alkali. Catalysts in general cause an increase in the yield of nitrous oxide for any given conditions, platinum-black being the most efficient catalyst in this respect, giving a yield up to 63 per cent. of the weight of hydroxylamine. The reaction probably proceeds through the formation of the labile condensation product, hydroxyhydrazine, which may react with a further mol. of hydroxylamine, giving ammonia and nitrogen: $3NH_2OH=NH_3+N_2+3H_2O$; or may decompose into ammonia and nitroxyl, the latter being converted into hyponitrous acid, which decomposes into nitrous oxide and water: $4NH_2OH=2NH_3+N_2O+3H_2O$.

Hydroxylamine in **oxygen** produces a white cloud without becoming hot. Hydroxylamine on filter paper or asbestos, in **air**, becomes heated owing to rapid oxidation; the free base absorbs oxygen from air, forming nitrous acid. The oxidation is favoured if traces of free alkali be present. Dil. aq. soln., free from salts, are fairly stable even if the temp. be raised; but conc. soln. were found by E. Divers and T. Shimidzu, W. Lossen, and E. Frémy to decompose readily on exposure to air. The aq. soln. decomposes more rapidly in the presence of sodium or potassium hydroxide; and V. Meyer and E. J. Constam found the presence of ammonia favours the decomposition so much so that an aq. soln. of hydroxylamine which had stood beside conc. aq. ammonia over-night was completely decomposed. S. S. Kolotoff said that the products of the decomposition are ammonia, nitrogen, nitrous oxide, water, and, added W. R. Dunstan and T. S. Dymond, nitrous acid. The reaction was examined by S. M. Tanatar, and V. Meyer. O. Löw said that the presence of platinum-black hastens the decomposition, and, added S. M. Tanatar, favours the formation of nitrous oxide. A. Findlay and W. Thomas found the vol. of gas evolved by an aq. soln. of hydroxylamine in the presence of colloidal platinum was much reduced in the presence of dextrin, starch, gelatin, peptone, and, to a less degree, of ferric hydroxide soln. and this the more the greater the proportion of dextrin, starch, or gelatin present. Thus, if v c.c. denotes the vol. of gas evolved in a given time, without and with the addition:

Time (minutes)	1	5	10	15	20	95	30	35	40
v	0·30	2·25	6·50	12·25	19·00	25·25	30·75	35·55	40·33
v 1% starch .	0·30	2·25	6·00	10·80	16·50	22·25	27·75	32·20	37·60
3% starch .	0·20	1·75	4·25	7·70	11·70	16·20	21·00	25·00	28·00

The colloidal addition thus retards the catalytic activity of the platinum possibly by adsorption of the colloid by the platinum. W. Strecker and H. Thienemann observed that hydroxylamine hydrate radily reacts with **ozone,** forming hydroxylamine nitrate. The reaction is not complete and an excess of ozone is needed.

According to C. A. Lobry de Bruyn, hydroxylamine is miscible with **water** in all proportions ; the aq. soln. has no smell ; and it reacts alkaline. When the aq. soln. is distilled, ammonia is evolved, and undecomposed hydroxylamine and water pass into the receiver without leaving any residue in the retort. E. Barrett studied the dissociation of the salts of hydroxylamine in aq. soln. A drop of hydroxylamine mixed with 5 c.c. of a 2·5 per cent. soln. of **hydrogen dioxide** gives off bubbles of gas, and the soln. contains nitric acid. C. Wurster found that the oxidation of hydroxylamine sulphate by hydrogen dioxide at 40° furnishes sulphuric acid, water, and a quantitative yield of nitric acid ; likewise also with hydroxylamine chloride. An aq. soln. of phenol, hydroxylamine salt, and hydrogen dioxide give nitrosophenol ; and phenylhydrazine is converted by hydrogen dioxide into benzene and diazobenzeneimide. S. M. Tanatar said that in neutral soln. the gas evolved is a mixture of equal parts of oxygen and nitrogen, and in alkaline soln. almost pure nitrogen. E. Francke also studied the action of hydrogen dioxide on hydroxylamine. A. Thum noted the formation of a hyponitrite in the oxidation of hydroxylamine by hydrogen dioxide.

According to C. A. Lobry de Bruyn, hydroxylamine inflames in a stream of **chlorine** gas ; **bromine** decomposes the base without incandescence, forming hydrogen bromide, nitrogen, and water ; and **iodine** acts in an analogous way. T. Haga represented the reaction with iodine: $2NH_2OH+2I_2=N_2O+4HI+H_2O$. According to K. A. Hofmann and F. Kroll, the oxidizing or reducing action of hydroxylamine depends on the conditions ; in feebly acidic soln., ferric chloride gives ferrous chloride and nitrous oxide, whereas in conc. sulphuric or phosphoric acid soln., ferrous sulphate gives ferric and ammonium sulphates. In acetic acid soln., hydroxylamine is oxidized by iodine, but not so in mineral acid soln., for in conc. hydrochloric acid, hydroxylamine liberates iodine from hydriodic acid. F. Raschig suggested that the first stage of the oxidation of hydroxylamine by iodine is the formation of *dihydroxylhydrazine*:

$$\begin{array}{l} \text{H—N—OH} \\ \text{H—}\dot{\text{N}}\text{—OH} \end{array}$$

which immediately passes into *dihydroxyldiimide,* HO.N : N·OH ; and this in turn into nitrous oxide, N_2O. C. T. Dowell found that an excess of chlorine on a soln. of hydroxylamine in carbon tetrachloride forms nitrogen trichloride. The base forms a salt when it reacts with **hydrochloric acid.** Hydroxylamine is vigorously oxidized by **sodium hypochlorite** ; W. R. Dunstan and E. Goulding studied the action of **hydriodic acid** and of the **metal iodides** on hydroxylamine. F. Raschig showed that the hypochlorites of sodium, potassium, and calcium are reduced by hydroxylamine salts and **iodic acid** is also reduced—according to E. Frémy, in acid or neutral soln. R. P. Sanyal and N. R. Dhar observed that in the reduction of iodic acid with hydroxylamine hydrochloride there is a period of induction, but the electrical conductivity of the system did not attain a maximum until after the appearance of the iodine ; this is attributed to the decomposition of the hydroxylamine in aq. soln. as well as to the oxidation of iodine. R. Möhlau and C. Hoffmann found that with a 10 per cent. soln. of **hypochlorous acid,** an aq. soln. is decomposed with the intermediate formation of NH_2OCl, **chlorohydroxylamine,** $NH_2OH+HOCl=NH_2OCl+H_2O$; and $2NH_2OCl=N_2+Cl_2+2H_2O$. F. Raschig said that hypochlorous acid can oxidize hydroxylamine completely to nitric acid. According to C. A. Lobry de Bruyn, no action occurs when **chlorates,** or **perchlorates** or **bromates** are mixed with hydroxylamine, but if a drop of sulphuric acid be present, the mixture inflames. The base reduces **iodates** and **periodates** without inflammation. D. Vitali represented the reduction of iodates by hydroxylamine sulphate by $2(NH_2OH)_2H_2SO_4+KIO_3=N_2O+N_2+6H_2O+KI+2H_2SO_4$; $2KI+H_2SO_4=K_2SO_4+2HI$; and $5HI+HIO_3=3I_2+3H_2O$; with bromates, bromine is separated only when the soln. is heated; and with chlorates, no reaction was observed. M. Schlötter represented the quantitative reduction of bromates in acid soln.: $4NaBrO_3+12NH_2OH=4NaBr+18H_2O+3O_2+6N_2$. The reaction was studied by A. Kurtenacker and J. Wagner, F. Fichter and W. F. Tschudin, and by E. Rupp and H. Mäder. According to P. Jannasch and A. Jahn, the reduction of the iodates, bromates, and chlorates occurs more readily in acid soln. than in neutral or ammoniacal soln. The reduction of the chlorates in ammoniacal soln. is very feeble. E. C. Gilbert observed that there is a variation in the reaction with hydroxylamine and an acidic soln. of potassium bromate depending on the order of mixing. G. R. Levi represented the reaction with equimolar parts of hydroxylamine hydrochloride and a **chlorite** in neutral soln.: $NH_2OH{\cdot}HCl+NaClO_2=NaCl+Cl+NO+2H_2O$; and with an excess of the hydroxylamine salt: $2NH_2OH.HCl+NaClO_2=NaCl+N_2O+3H_2O+2HCl$. Powdered **sulphur** does not react with hydroxylamine. S. M. Tanatar, and F. Raschig noted that **sulphur dioxide** is oxidized to ammonium sulphate, and F. Raschig obtained hydroxylamine sulphaminates by the action of sulphur dioxide on hydroxylamine salts—*vide* sulphur dioxide. The **persulphates** are reduced by hydroxylamine salts. A. Gutmann represented the reaction with **sodium tetrathionate**, in acid soln. by $H_2S_4O_6+NH_2OH+H_2O=2H_2SO_4+2S+NH_3$; and in alkaline soln. by $Na_2S_4O_6+2NH_2OH+3NaOH=2Na_2S_2O_3+NaNO_2+3H_2O+NH_3$. O. Hinsberg found that **selenium dioxide** is reduced to selenium by aq. soln. of the base. According to C. A. Lobry de Bruyn, **ammonia** is absorbed to the extent of 20 per cent. by molten hydroxylamine; and S. S. Kolotoff observed no reaction when ammonia is heated for 100 hrs. in a sealed tube with hydroxylamine at 100°. For the action of **hydrazine**, *vide infra*. **Nitrous oxide** and **nitric oxide** are without action on the base, but liquid nitrous oxide is reduced. G. Oesterheld, and E. J. Joss represent the reaction with **hyponitrous acid**: $H_2N_2O_2+2NH_2OH=2N_2+4H_2O$. According to V. Meyer, **nitrous acid** decomposes an aq. soln. of the base: $NH_2OH+HNO_2=2H_2O+N_2O$. S. M. Tanatar found the reaction between hydroxylamine chloride and sodium nitrite occurs with difficulty in the presence of magnesia, calcium oxide or carbonate, and cadmium or zinc oxide; if the acid soln. of the hydroxylamine chloride be neutralized, it does not react with sodium nitrite. The reaction with hydroxylamine sulphate and nitrite is spontaneous and vigorous in conc. soln.; in dil. soln., the reaction is very slow with cold soln. W. Wislicenus, and C. Paal showed that some hyponitrous is formed as an intermediate product of the reaction, and it can be isolated, particularly, said S. M. Tanatar, if chalk be present in the system. C. Montemartini measured the speed of the reaction between hydroxylamine chloride and sodium nitrite: $NH_2OH{\cdot}HCl+NaNO_2=N_2O+NaCl+2H_2O$. If k be the velocity constant; C (grams. per 100 c.c.), the conc. of the hydroxylamine t minutes from the beginning; and C_0 the conc. at the beginning when $t=0$, $dC/dt=kC^2$, and $k=(C^{-1}-C_0{}^{-1})t^{-1}$. If C_0 be greater than 0·036 at 16°, k increases with time, and when $k=0{\cdot}226$, at 25°, it remains nearly constant. When t is greater than 400, the value of k decreases. The presence of either sodium sulphate or sodium chloride decreases the speed of the reaction considerably, as shown by the decreased values of k. The product $K\eta$ is not constant for soln. with varying amounts of sodium chloride—here η denotes the viscosity constant of the soln., but $k\eta^2$ is approximately constant when 16–24 per cent. of sodium chloride or 8–14 per cent. of sodium sulphate is present. If n denotes the ratio of the number of mols. of the one salt—hydroxylamine chloride—sodium chloride—then kn was not constant. With hydroxylamine hydrochloride, the velocity of the reaction is less than when the sulphate is used, and still less than with the nitrate. With lithium, sodium, and potassium nitrites, k decreases as the at. wt. of the metal increases, and k is greater for strontium nitrite than for that of barium. Hydroxylamine probably reduces nitric acid: $2HNO_3+2NH_2OH=2HNO_2+N_2O+3H_2O$.

According to C. A. Lobry de Bruyn, no reaction occurs when hydroxylamine is mixed with ordinary **phosphorus**. Hydroxylamine hydrochloride reacts slowly with **phosphorus pentachloride** in the cold, but at 100°, the action is energetic—hydrogen chloride is given off, and ammonium chloride and some nitrogen are formed. Inflammation occurs when the base is mixed with **phosphorus trichloride** or the pentachloride. E. Ebler studied the action of hydroxylamine chloride on soln. of **arsenic acid,** and on **bismuth salts**; A. Gutmann said that with **sodium arsenite** the reaction is symbolized: $NH_2OH+Na_3AsO_3=Na_3AsO_4+NH_3$, with the side reaction: $3NH_2OH=NH_3+N_2+3H_2O$. Hydroxylamine does not react with **carbon monoxide,** but **carbon dioxide** is absorbed in great quantities with a slight rise of temp., and the formation of a liquid which does not freeze at —10°. **Carbon disulphide** unites with hydroxylamine, forming a substance which slowly becomes yellow, then orange, and there is then a separation of sulphur. Hydroxylamine is miscible in all proportions with **methyl or ethyl alcohol,** and the conc. soln. on cooling may deposit acicular or scaly crystals; it is slightly soluble in **propyl alcohol**; boiling **ether** dissolves about 1·2 per cent. of the base, and on cooling needle-like crystals separate; **acetic ether** dissolves 1·6 per cent. of the base at ordinary temp.; and **chloroform,** 0·3 per cent. With chloroform, a white amorphous compound with hydroxylamine is formed. Hydroxylamine is virtually insoluble in **benzene** or **petroleum ether.**

The action of hydroxylamine or its salts on *carbonyl* compounds was studied by S. F. Acree and co-workers; on *acetone,* by P. Landrieu, and I. Schöttle; on *ketones,* by R. Ciusa and A. Terni, P. I. Petrenko-Kritschenko and S. Lordkipanidze, C. Moureu and I. Lazennec, G. Minunni and C. Carta-Satta, and A. Janny; on *ethylene oxide,* by L. W. Jones and G. R. Burns; on *cyanogen bromide,* by H. Wieland and H. Bauer; on *potassium ferrocyanide,* by K. A. Hofmann and H. Arnoldi, and A. Thum; on *nitro-prussides,* by J. Giral-Pereira, and J. G. Pereira; on *santonin,* by L. Francesconi and G. Cusmano; on *fats,* by E. Morelli; on *dimethylpyronedicarboxylate,* by C. Palazzo; on *peroxydase,* by A. Bach; on *cyanoamides,* by J. von Braun and R. Schwarz; on *unsaturated acids,* by T. Posner, and C. D. Harries and W. Haarmann; on *bromonitrocamphane,* by M. O. Forster; on *aldehydes,* by K. Hess and C. Uibrig; on *oxaloacetic acid,* by H. J. H. Fenton and H. O. Jones; on *formic acid,* by G. Schröter and M. Peschkes; on *ethyl phenylpropionate,* by S. Ruhemann and H. E. Stapleton; on *methyl, ethyl, and propyl iodides,* by W. R. Dunstan and E. Goulding, A. Hantzsch and W. Hilland, and C. A. Lobry de Bruyn; on *thiocarbamide,* by W. R. G. Atkins and E. A. Werner, and E. Tiemann; on *phenyl carbamide,* by E. O. Beckmann; on *trinitrotoluene,* by M. Giua; on *nitrosobenzene,* by E. Bamberger and E. Renauld; on *nitrobenzene,* by A. Angeli, and E. Bamberger and E. Knecht; on *acetamide,* by M. O. Forster; on *ethyl formate,* by G. Schröter; on *lactones,* by L. Francesconi and G. Cusmano; on *coumarins,* by T. Posner and R. Hess; on *acetylene,* by E. Oliveri-Mandala; on *lutidone,* by I. Schöttle; on *benzoylhydracetic acid,* I. Schöttle; on *benzene sulphonate,* by A. Seyewetz and L. Poizat; on *phenyl hydrazine,* by E. Fischer; on *zinc ethyl* and *magnesium alkyl halides,* by F. Ebler and R. L. Krause; on *metaphosphoric esters* and *phosphorous esters,* by W. Strecker and H. Heuser; etc.

C. A. Lobry de Bruyn found that **sodium** reacts with hydroxylamine with incandescence; in ethereal soln., hydrogen is developed and a white, voluminous, hygroscopic **sodium hydroxylamite,** NH_2ONa, is formed, which sometimes catches fire when exposed to air. E. Ebler and E. Schott found that when hydroxylamine is treated with calcium filings at 50°, a white powder of **calcium hydroxylamite,** $Ca(ONH_2)_2$, is formed which explodes at 180°. It is slowly hydrolyzed by moist air, and reacts with water: $Ca(ONH_2)_2+2H_2O=Ca(OH)_2+2NH_2OH$—*vide infra.* C. A. Lobry de Bruyn reported that no reaction occurs with hydroxylamine and **magnesium** powder. D. Vitali found that magnesium acts on a soln. of hydroxylamine chloride, forming hydroxylamine and hydrogen. According to E. Ebler and E. Schott, the base is reduced when heated with *zinc* dust, forming zinc oxide and ammonia; sometimes the mixture inflames, at other times it explodes. The immediate product of the reaction is not $ZnO : NH_3$, but rather **zinc hydroxylamite,**

$Zn(ONH_2)_2.3NH_2OH$. This salt can be purified by recrystallization from absolute alcohol. When partially immersed in hydrazine hydrate, and partially exposed to air, it gives off hydrogen, and forms **zinc hydrazinocarboxylate dihydrazinate,** $(NH_2.NH.CO.O)_2Zn(NH_2NH_2)_2$. It does not give a precipitate with a soln. of a chloride of an alkaline earth; and when the soln. is boiled, the substance is hydrolyzed, and the carbonate of the alkaline earth is precipitated. There are also indications of the formation of very unstable **ferrous hydroxylamite** by the action of **iron** on hydroxylamine salts.

C. A. Lobry de Bruyn found that molten hydroxylamine does not react with solid **sodium hydroxide,** but dissolves therein, forming a mass which attracts oxygen from the air. W. Lossen showed that the alkali hydroxides react with an aq. or alcoholic soln. of the hydroxylamine salts liberating hydroxylamine which then reacts with the excess of alkali-lye, forming ammonia, nitrous oxide, and nitrogen. According to M. Berthelot, M. Berthelot and G. André, the main reaction is symbolized: $3NH_2OH=NH_3+N_2+3H_2O$, and there is at least one side reaction: $4NH_2OH=2NH_3+N_2O+3H_2O$—the gaseous product contains about 95 per cent. of nitrogen and 5 per cent. of nitrous oxide. The thermal value of the first reaction is 57 Cals. per mol, and of the second, 45·2 Cals. If platinum black be employed as catalyst, the side reaction predominates and becomes the main reaction, for the gaseous product then contains 15 per cent. of nitrogen and 85 per cent. of nitrous oxide. In neutral solutions, hydroxylamine decomposes very slowly. A. Thum found that hydroxylamine is oxidized by **cupric oxide,** and E. Francke studied the reaction with the copper oxides in some detail. C. A. Lobry de Bruyn said that hydroxylamine is inflamed in contact with **barium oxide**; W. Lossen, that **barium hydroxide** reacts with aq. or alcoholic soln. of hydroxylamine salts as in the case of the alkali hydroxides. K. A. Hofmann and V. Kohlschütter digested finely powdered **calcium oxide,** or **calcium carbide** with a soln. of hydroxylamine in methyl alcohol, and obtained a white powder, which is partly decomposed by water at ordinary temp. into calcium hydroxide and hydroxylamine, and which reduces ammoniacal soln. of copper or silver salts. E. Ebler and E. Schott regard the product as a mixture of calcium hydroxylamite and hydroxide. W. Lossen found that **magnesium oxide** does not decompose a soln. of hydroxylamine chloride at ordinary temp., but when warmed, ammonia gas is vigorously evolved. C. A. Lobry de Bruyn said that a mixture of hydroxylamine with **barium or lead dioxide** inflames.

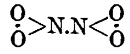
Hydroxylamine was found by C. A. Lobry de Bruyn to dissolve many salts—**potassium iodide, bromide, and cyanide** are copiously dissolved; while **sodium or barium nitrate,** and **sodium or potassium chloride** are dissolved to the extent of 11–14 per cent. The soln. of barium nitrate and **potassium sulphate** in hydroxylamine do not give a precipitate of barium sulphate when they are mixed. F. L. Hahn and K. Brunngässer found that the solubility of **barium carbonate** is increased more than 30-fold in $0{\cdot}25M$-NH_2OH. Hydroxylamine can unite with many salts, forming compounds in which it appears to act as **hydroxylamine of crystallization** like water in hydrated salts—*e.g.* L. Crismer prepared $ZnCl_2.2NH_2OH$, $CdCl_2.2NH_2OH$, and $BaCl_2.2NH_2OH$; H. Alexander, $PtCl_2.2NH_2OH,Pt(OH)_2.4NH_2OH$, and $PtSO_4.4NH_2OH.H_2O$; H. Goldschmidt and K. L. Syngros, compounds with the carbonates of zinc, iron, manganese, and nickel; W. Feldt, compounds with cobalt and manganese salts; and R. Uhlenhuth, $NiSO_4.6NH_2OH$. A number of **complex salts** have been made, thus, W. Meyeringh prepared $(NH_3OH)Al(SO_4)_2.12H_2O$; $(NH_2OH)Cr(SO_4)_2.12H_2O$; and $(NH_2OH)Fe(SO_4)_2.12H_2O$. A double salt is formed with magnesium sulphate, $Mg(NH_3OH)_2(SO_4)_2.6H_2O$, but not with ferrous and zinc sulphates or with magnesium and manganese chlorides. G. Antonoff has described a number of these salts with magnesium and the alkaline earth chlorides. Hydroxylamine is **amphoteric** in that it behaves towards the alkalies like a weak acid, forming **hydroxylamites,** and towards the bases like ammonia, forming a series of **salts.** Hydroxylamine generally acts as a **reducing agent**, particularly in acid soln., but as shown by A. Piccini, L. Marino, and S. M. Tanatar, it can also act as an **oxidizing agent**, for in alkaline soln. it oxidizes the alkali nitrites, nitric oxide, and the hyponitrites ; and in acid soln. stannous chloride forms stannic chloride; sulphurous acid gives ammonium sulphate ; and sulphuric acid soln. of vanadium trioxide are converted to vanadium tetroxide.

C. A. Lobry de Bruyn found that anhydrous **copper sulphate** causes hydroxylamine to inflame, and the hydrated salt is vigorously reduced. W. Lossen, E. Ebler, G. von Knorre and K. Arndt, E. Francke, H. O. Jones and F. W. Carpenter, E. Péchard, W. Feldt, A. Thum, C. Kjellin, W. Meyeringh, and E. Frémy noted the reduction of soln. of copper salts by hydroxylamine. The precipitate first formed is grass-green, and it then becomes copper-red and forms a colourless soln. with an excess of hydroxylamine, without the evolution of a gas. When the soln. is exposed to air, the surface acquires a dirty bluish-green separation which again passed into soln. when the liquid is agitated. When the soln. is heated, a gas is evolved, and if it be mixed with a little alkali-lye, or baryta-water, it furnishes an orange-yellow precipitate, probably of cuprous hydroxide. Alkaline soln. of copper oxide give a precipitate of cuprous hydroxide with hydroxylamine. J. Donath said that almost all the nitrogen is evolved as nitrous oxide, very little ammonia is formed. Ammoniacal soln. of copper oxide are decolorized by hydroxylamine and alkali-lye, giving a yellow precipitate when treated with alkali-lye. The precipitate obtained by adding an alcoholic soln. of hydroxylamine to a soln. of copper sulphate is less variable than that produced by an aq. soln. The first precipitate is grass-green, it then changes to dark azure-blue with an excess of hydroxylamine. When dried over sulphuric acid, the precipitate is green, and when boiled with water, it gives off a gas and forms cuprous oxide. A. Kurtenacker and F. Wengefeld found that copper sulphate in acidic soln. of hydroxylamine yields mainly nitrous and nitric oxides and a little nitrogen ; in strongly alkaline soln., nitrous oxide is the main product. Powdered **silver nitrate** was found by C. A. Lobry de Bruyn to be reduced by hydroxylamine, forming silver. A. Lainer, E. Ebler, W. Lossen, and E. Frémy said that aq. soln. of silver salts are reduced to metal by soln. of hydrazine salts. The precipitate first obtained is black, and this soon gives off gas copiously and is transformed into the metal. W. Lossen, and E. Ebler found that a soln. of **gold chloride** is likewise reduced to metal by hydroxylamine salts.

W. Lossen observed that no precipitation occurs when a soln. of hydroxylamine is added to one of a **calcium, strontium, barium, or magnesium salt.** A soln. of **zinc sulphate** gives a precipitate not soluble in an excess of the hydroxylamine soln. E. Ebler studied the action of the chloride on cadmium salts. C. A. Lobry de Bruyn found that anhydrous hydroxylamine has no perceptible action on the anhydrous sulphates of zinc or magnesium. W. Lossen, E. Ebler, and E. Frémy observed that hydroxylamine soln. has a strong reducing action on **mercury salts.** The precipitate with mercuric chloride is at first yellow ; it then rapidly changes into mercurous chloride ; and if excess of hydroxylamine be present, it gives off gas, leaving mercury as a residue. M. Adams prepared mercury compounds with hydroxylamine analogous to the mercuriammonium compounds (**4.** 31, 31). N. R. Dhar studied the induced reaction involving the effect of hydroxylamine on the reduction of mercuric chloride by oxalic acid. Soln. of **aluminium salts,** say alum, give precipitates with an aq. soln. of hydroxylamine, insoluble in an excess of precipitant—*vide supra,* hydroxylamine—alum. According to A. Benrath and K. Ruland, **ceric sulphate** in the presence of sulphuric acid oxidizes hydroxylamine to nitrogen and nitrous oxide (69 to 73 per cent.). E. Ebler studied the action of hydroxylamine hydrochloride on **tin salts.** C. Kjellin found that **stannous hydroxide** and hydroxylamine react in accord with the equation: $Sn(OH)_2+NH_2OH+H_2O=Sn(OH)_4+NH_3$. W. Lossen noted that soln. of **lead salts**—*e.g.* lead acetate—give a precipitate with hydroxylamine not soluble in an excess. A. Gutmann represented the oxidizing action of hydroxylamine on **sodium arsenite :**

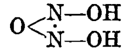
$NH_2OH+Na_3AsO_3=Na_3AsO_4+NH_3$, which runs concurrently with $3NH_2OH=NH_3+N_2+3H_2O$. E. Ebler, G. von Knorre and K. Arndt, and K. A. Hofmann and F. Küspert observed that **vanadium pentoxide** is reduced by hydroxylamine with the evolution of nitrogen; as indicated above, hydroxylamine was found by A. Piccini to oxidize a sulphuric acid soln. of **vanadium trioxide** into the tetroxide. According to A. Kurtenacker and F. Werner, alkaline soln. of hydroxylamine are reduced quantitatively to ammonia by vanadyl salts, quinquevalent molybdenum salts, and ferrous sulphate. In dil. acidic soln., cuprous sulphate and molybdenum sulphate have the same effect, ferrous sulphate and cuprous chloride are without action, and vanadyl sulphate causes a catalytic decomposition into ammonia, nitrogen, and nitrous oxide. In very strongly acidic soln., only the molybdenum salt has any action, causing a slow but eventually complete reduction to ammonia. Cuprous oxide induces a slow catalytic decomposition of alkaline hydroxylamine soln., the velocity of the action increasing with the alkalinity. K. A. Hofmann and V. Kohlschütter prepared a complex salt with **metavanadic acid**; a drop of anhydrous hydroxylamine on powdered **potassium dichromate** produces a violent explosion; **ammonium dichromate** and chromic acid act a little less vigorously. F. Raschig noted that chromic acid and the chromates are reduced by soln. of hydroxylamine salts. According to A. Thum, a cold, neutral soln. of **potassium chromate** is not changed by a soln. of hydroxylamine, but when heated, the colour darkens, and if a little sulphuric acid be present, gas is evolved and a brown precipitate is formed; if more acid be added, the precipitate dissolves. G. von Knorre and K. Arndt found that with mercuric chloride in alkaline soln., nitrous oxide and nitrogen are formed, and nitrites are produced. A. Kurtenacker and F. Wengefeld showed that in the oxidation of hydroxylamine by potassium dichromate in weak acid soln., half the hydroxylamine is oxidized to nitric acid, and the proportion of nitric oxide increases, and that of nitrous oxide decreases as the acidity of the soln. is diminished; in strong acid soln., the proportion of hydroxylamine oxidized to nitric acid sinks to about 25 per cent. and the gas produced is nitrous oxide; and in alkaline soln., the formation of nitric acid is still further reduced, while the gaseous products are nitrogen and nitrous oxide. The oxidation of hydroxylamine is complete only in weak acidic soln.; in alkaline soln., it varied from 47 to 64 per cent., and in strong acid soln., it was about 78 per cent. E. Francke studied the oxidizing action of chromic oxide on hydroxylamine. G. von Knorre and K. Arndt, G. Bertoni, W. Meyeringh, and W. O. de Coninck found that nitrous fumes and nitrogen gases are evolved; and W. Lossen, that **chrome-alum** gives a precipitate with a soln. of hydroxylamine, not soluble in an excess of the precipitant. W. Meyeringh prepared hydroxylamine chrome-alum. According to K. A. Hofmann and V. Kohlschütter, **molybdic, tungstic, and uranic acids,** or **molybdates, tungstates, and uranates,** form complexes with hydroxylamine. The action of hydroxylamine hydrochloride on molybdates and tungstates was examined by E. Ebler. A. Kurtenacker and F. Wengefeld said that molybdic acid has no action on hydroxylamine in alkaline soln., but in acidic soln. it acts catalytically, forming ammonia, nitrogen, and nitrous and nitric oxides. According to A. Kurtenacker and R. Neusser, the decomposition of hydroxylamine in the presence of a vanadate in acid soln. yields nitrogen and nitrous oxide, the proportion of the latter first decreasing and then increasing with decreasing acidity. The simultaneous reduction of the vanadate takes place. In neutral soln., nitrous oxide only is produced, but in alkaline soln. a catalytic decomposition to nitric and nitrous oxides and nitrogen takes place, the proportions of the first two decreasing with increasing alkalinity. The oxygen in these gases must be derived from the hydroxylamine, and the latter is reduced to ammonia. When the vanadate is replaced by ammonium molybdate, nitric oxide, nitrogen, and nitrous oxide are produced, the first-named decreasing in amount as the soln. passes from the acid to the alkaline state. The evolution of gas corresponds with about half the hydroxylamine used; the molybdates behave like the vanadates in strongly alkaline soln. A. Kurtenacker and F. Wengefeld found that quinquevalent molybdenum, quadrivalent vanadium, and bivalent iron reduced hydroxylamine to ammonia.

C. A. Lobry de Bruyn found that when solid hydroxylamine is brought into contact with solid **potassium permanganate,** there is immediately produced a white flame. F. Raschig suggested that the oxidation of hydroxylamine in dil. sulphuric acid soln. by potassium permanganate passes successively through the stages: *dihydroxylhydrazine,* 2(HO).NH.NH(OH), *vide supra,* iodine—dihydroxyldiimide, nitrous oxide and an *iso*-nitrogen tetroxide, which would have the constitution:



$$\begin{matrix}O\\ \vdots\\ O\end{matrix}\!>N.N<\!\begin{matrix}O\\ \vdots\\ O\end{matrix}$$

and which, on hydrolysis, yields nitric acid and nitrogen: $5N_2O_4+4H_2O=8HNO_3+N_2$. Complete oxidation to nitric acid cannot be effected with the permanganate. In a dil. alkaline soln., F. Raschig suggested that *tetrahydroxylhydrazine,* $(HO)_2N.N(OH)_2$, is formed and immediately broken down into nitrous oxide and nitrite. A. Kurtenacker and R. Neusser observed that the products of the reaction are greatly influenced by the acidity or alkalinity of the soln., and to a less extent by the conc. In acidic or strongly alkaline soln., potassium permanganate oxidizes hydroxylamine to nitrous oxide, and nitric acid or a nitrate, but in slightly alkaline soln., some nitrogen is produced. C. A. L. de Bruyn found that anhydrous **manganese sulphate** has no perceptible action on hydroxylamine—*vide* the nitrate and sulphate of hydroxylamine. C. Kjellin found that the amount of ammonia produced by the action of **manganese hydroxide** on hydroxylamine is negligibly small. W. Feld prepared a complex salt with manganese sulphate. Alkaline soln. of potassium permanganate are reduced by hydroxylamine salts, and A. Thum said that the hydroxylamine is converted into nitrohydroylaminic acid:

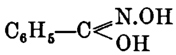


$$O<\!\begin{matrix}N{-}OH\\ \vdots\\ N{-}OH\end{matrix}$$

as an intermediate product of the oxidation. The reaction was studied by E. Francke. F. Raschig, and S. M. Tanatar found that soln. of **ferric salts** are reduced to ferrous salts by hydroxylamine salts, though W. Meyeringh was able to prepare a hydroxylamine ferric-alum. A. Kurtenacker and R. Neusser found that the sole oxidation product with ferric salts in acidic soln. is nitrous oxide, but the action is not complete unless the ferric salt is present in considerable excess. In neutral soln., a little nitrogen is produced, but in alkaline soln., the ferrous hydroxide formed is oxidized by the hydroxylamine. A. Kurtenacker and F. Wengefeld found the ferric hydroxide produces nitrous oxide and ammonia, catalytically in alkaline soln. E. Francke, W. R. Dunstan and T. S. Dymond, and F. Haber showed that if **ferrous hydroxide** be suspended in alkali-lye or in an ammoniacal soln., the hydroxylamine is reduced to ammonia, and red ferric hydroxide is formed. If the product be dissolved in acid and treated with hydroxylamine, the ferric salt is reduced back to the ferrous state. E. Ebler and E. Schott did not agree with F. Haber, but the discrepancy is attributed to F. Haber having used dil. soln. C. Kjellin represented the reaction: $H_2O+NH_2OH+2Fe(OH)_2=NH_3+2Fe(OH)_3$. W. Lossen observed that **ferrous salts** give a precipitate with an aq. soln. of hydroxylamine, which is insoluble in an excess of the precipitant; A. D. Mitchell said that the reaction, after the early stages, is directly proportional to the conc. of the hydroxylamine and to the square of the conc. of the ferric chloride, and inversely proportional to the conc. of the ferrous salt, and to the square of the H-ion conc. It is assumed that the reaction is: $2Fe^{\cdot\cdot\cdot}+NH_3OH^{\cdot}\rightleftharpoons Fe^{\cdot\cdot}+2H^{\cdot}+(NOH,Fe,H)^{\cdot\cdot\cdot}\rightarrow N_2O$, etc., where the bracketed term represents an intermediate complex. The temp. coeff., 6·5 per 10°, is abnormally high. The salt effect is negative, for the speed of the reaction is depressed by the addition of indifferent salts. W. Lossen observed that hydroxylamine gives a precipitate, insoluble in excess, when added to a soln. of **nickel sulphate.** R. Uhlenhuth prepared a complex salt. C. A. Lobry de Bruyn found that anhydrous hydrazine is without action on anhydrous nickel sulphate, but anhydrous **cobalt sulphate** is transformed into a voluminous brown mass. W. Feldt prepared a complex salt with cobalt sulphate. According to E. Frémy, and W. Lossen, a prolonged heating is necessary for an aq. soln. of hydroxylamine to reduce a soln. of platinum tetrachloride to the metal. H. Alexander prepared some complexes with platinum salts and hydroxylamine—*vide supra.*

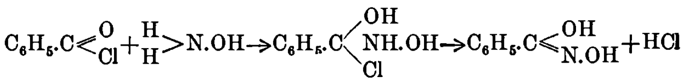
Some reactions of analytical interest.—The reactions of hydroxylamine are in many cases quite distinctive and are shown by relatively small quantities of the compound; hence, they can be used for its identification. Hydroxylamine can be detected by its reducing action on alkaline or ammoniacal soln. of copper oxide, since it forms a red precipitate of cuprous oxide recognizable, it is said, if but one part of hydroxylamine be present in 100,000 parts of water. A. Angeli proposed to neutralize the soln. with either hydrochloric acid or sodium hydroxide; add about a milligram of sodium nitroprusside to about 2 c.c. of soln. in a test-tube; make the soln. alkaline with about 1 c.c. of N-NaOH; shake; and warm the soln. rapidly to 100° on a water-bath. The presence of as little as 0·01 per cent. of hydroxylamine will give a magenta coloration. W. C. Ball said that if hydroxylamine is boiled with a drop of yellow ammonium sulphide until sulphur begins to separate, and then mixed with 2 or 3 c.c. of conc. aq. ammonia and the same vol. of alcohol, a purple-red coloration sensitive to one part of hydroxylamine in 500,000 parts of soln. will appear. Hydrazine does not show any coloration under the same conditions. E. Bamberger, and G. W. Pucher and H. A. Day, treated soln. with sodium acetate and benzoyl chloride when hydroxylamine forms benzhydroximic acid which gives a violet-red coloration with ferric chloride. W. M. Fischer said that 0·00005 per cent. of hydroxylamine in the presence of ammonium or hydrazine salts can be detected by adding 1–2 drops of 2½ per cent. yellow ammonium sulphide soln., and 1–2 c.c. of ammonia to 1–5 c.c. of the soln. to be tested. In presence of hydroxylamine an unstable purple colour is developed in the soln. on shaking in presence of air, and its appearance is greatly accelerated by adding 1–2 drops of 0·1N-manganous sulphate soln. which appears to act as an oxidizing catalyst. W. N. Hirschel and J. A. Verhoeff said that an ammoniacal soln. of diacetylmonoxime in presence of hydroxylamine condenses to dimethylglyoxime, which in presence of nickel gives the well-known red precipitate. A conc. of 1 mg. per c.c. of hydroxylamine gives the precipitate at once in the cold; for small quantities, it is necessary to boil, cool, and neutralize with acetic acid, and in this way 0·01 mg. can be detected. C. A. Lobry de Bruyn determined the free hydroxylamine in aq. soln., by titration with standard acid, using methyl orange as indicator. Hydroxylamine can be determined in a soln. by adding a known amount of a substance—*e.g.* ferric sulphate (W. Meyerlingh, A. Leuba, F. Raschig, and L. Amat); vanadic sulphate (K. A. Hofmann and F. Küspert); silver nitrate (G. Denigès); or titanium trichloride (A. Stähler, W. C. Bray and coworkers, and E. Knecht)—and determining volumetrically the amount which has not been reduced in the remaining soln. adding an excess of permanganate soln., and back titrating with arsenious acid (A. Thum, and K. A. Hofmann and F. Küspert). It is also determined by titration with a standard soln. of potassium permanganate after the addition of sodium oxalate (L. J. Simon); and by titration of the alkaline soln. with mercury acetamide (M. O. Forster). H. O. Jones and F. W. Carpenter poured the hydroxylamine into an ammoniacal soln. of copper oxide, or one of copper potassium carbonate (A. Soldaini). The mixture was boiled and the precipitated cuprous oxide filtered, washed, and added to a soln. of ferric-alum in a flask filled up with carbon dioxide. The resulting ferrous sulphate was titrated with potassium permanganate.

The constitution of hydroxylamine.—Analyses, and the mol. wt. determination by the f.p. method agree with the empirical formula NH_3O, which may be represented graphically by $H_3{\equiv}N{=}O$, or $H_2{=}N{-}OH$, according as the nitrogen be quinque- or tervalent. It is generally supposed that hydroxylamine has a constitution related to that of ammonia, with but one hydrogen atom of the ammonia replaced by hydroxyl. This agrees with its formation from nitric acid: $HO{-}NO_2+6H\rightarrow HO{-}NH_2+2H_2O$; a reaction analogous with the formation of amine bases from the nitro-compounds $R{-}NO_2+6H\rightarrow R{-}NH_2+2H_2O$; and, like the amines and ammonia, hydroxylamine unites directly with acids to form salts. If hydroxylamine be constituted $H_2{=}N{-}OH$, the hydrogen atoms are not of equal value, since one is not related to the nitrogen atom the same as the other two. Consequently, the compound might be expected to yield two different substitution products, according as the hydrogen of the hydroxyl group or the hydrogen of the amido- or NH_2-group be replaced by an eq. radicle. H. Remy, and H. Henstock discussed the electronic structure. W. Lossen worked for many years *Ueber die Strukturformel des Hydroxylamins und seiner amidartigen Derivate.* At first, it was thought that just as the acid chlorides—like benzoyl chloride, $C_6H_5CO.Cl$—react with ammonia, forming acid amides—like benzamide, $C_6H_5CO.NH_2$—as symbolized: $C_6H_5CO.Cl+2NH_3\rightarrow C_6H_5CO.NH_2+NH_4Cl$, so do acid chlorides react with hydroxylamine, giving what are called **hydroxylamic acids**—*vide infra*—or, as A. Werner prefers to call them, **hydroxamic acids**—for example, with benzoyl chloride, *benzhydroximic acid*, $C_6H_5CO.HNOH$, is formed: $C_6H_5CO.Cl+2NH_2OH \rightarrow C_6H_5CO.NH_2O+NH_2OH.HCl$. From this point of view, the hydroximic acids bear the same relation to hydroxylamine as the acid amides bear to ammonia. By a similar reaction, a second and third group have been introduced into hydroxylamine, forming the di- and tri- substituted hydroxylamines. By boiling these substituted compounds with dil. hydrochloric acid, hydroxylamine is restored. *Dibenzhydroximic acid* should have two isomeric forms in accord with the fact that there are two kinds of hydrogen atoms in hydroxylamine—namely $RH{=}N{-}OR$ and $R_2{=}N{-}OH$—and in agreement with this, two forms were found to exist. All this agrees better with the formula $H_2{=}N{-}OH$ than with $H_3{\equiv}N{=}O$; but the different isomers of the tri-substituted acids weakened confidence in the argument. Only one form of *tribenzhydroxylamine*, $(C_6H_5)_2N.OC_6H_5$, should be possible, whereas three isomers are known to exist; again, two *dibenzanisyl-hydroxylamines* are theoretically possible—$R_bR_a{=}N{-}OR_b$ and $R_bR_b{=}N{-}OR_a$—whereas three have been actually found. Consequently, either the fundamental assumption as to the constitution of hydroxylamine is wrong, and each of the three hydrogen atoms has a different substitution value, or else the constitution of the base changes when its hydrogen atoms are replaced by three radicles, so that each of the three nitrogen valencies acts in a different manner. In later years, W. Lossen came to the latter conclusion; he supposed that the monosubstitution product has a constitution typified by



$$C_6H_5{-}C{<}\begin{smallmatrix}N.OH\\OH\end{smallmatrix}$$

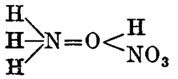
and not by $C_6H_5.CO.NH.OH$. The two tautomeric forms suggested by the first two formulæ have not been discovered, and the experimental evidence does not decide which of the two is preferable, for, as N. V. Sidgwick has said: "There are arguments of no great weight on either side." With either structure, it follows that the hydroximic acids are not formed by reactions analogous with the action of acid chlorides on ammonia. In each case, a transient addition product is probably first formed, and this breaks down into hydroximic acid and hydrogen chloride, thus:



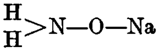
$$C_6H_5.C{<}\begin{smallmatrix}O\\Cl\end{smallmatrix}+\begin{smallmatrix}H\\H\end{smallmatrix}{>}N.OH\rightarrow C_6H_5.C\begin{smallmatrix}OH\\NH.OH\\Cl\end{smallmatrix}\rightarrow C_6H_5.C{<}\begin{smallmatrix}OH\\N.OH\end{smallmatrix}+HCl$$

In this manner, it can be seen that although the three replaceable hydrogen atoms may appear to have a different position in the mol., the cases of isomerism, inexplicable on the first hypothesis, can be readily explained without assuming that hydroxylamine itself has a structure different from that generally accepted, viz. $H_2{=}N{-}OH$. The subject was discussed by A. Hantzsch and A. Werner, R. Behrend and E. König, K. Auwers and V. Meyer, L. W. Jones, and A. Michael.

S. S. Kolotoff supposed that because he could not make the reaction $NH_2OH+NH_3\rightarrow N_2H_4+H_2O$ progress by heating the mixture under different conditions, hydroxylamine does not contain a hydroxyl group. This argument does not appear to have much weight. E. Wagner tried to explain the oxidizing and reducing properties of hydroxylamine by assuming it to be derived from hydrogen dioxide by the substitution of one hydroxyl group by one amido-group. This would make the formula of hydroxylamine depend upon that of hydrogen dioxide. If the latter be $HO{=}OH$, that of hydroxylamine may be supposed to be $H_2N{\equiv}OH$; and if $H_2{=}O{=}O$, hydroxylamine may be supposed to be $H_3N{=}O$. The optical measurements of R. Bach, and J. W. Brühl make the formula $H_2N:NH_2$ for hydrazine and of $H_2N{=}OH$ for hydroxylamine improbable. E. Ebler and E. Schott have brought forward evidence to show that both the constitutional formulæ $H_2{=}N{-}OH$ and $H_3{\equiv}N{=}O$ may be correct under special conditions. Thus, F. Haber regarded hydroxylamine to be constituted $H_2{=}N{-}OH$ when it acts as a reducing agent; and as $H_3{=}N{=}O$ when it acts as an oxidizing agent. E. Ebler and E. Schott concluded that there is a kind of desmotropism. **In alkaline solutions, hydroxylamine plays the rôle of an amido-acid $H_2{=}N{-}OH$, and acts as a reducing agent; while in acid solutions, it behaves like basic ammonia oxide $H_3{\equiv}N{=}O$, and acts as an oxidizing agent.** In the latter case, hydroxylamine salts resemble the oxonium compounds in containing a quadrivalent oxygen atom.

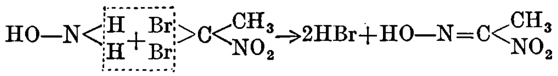

$\begin{matrix}H\\H\\H\end{matrix}{>}N{=}O{<}\begin{matrix}H\\NO_3\end{matrix}$

Hydroxylamine nitrate.
[Hydroxylamine a base.]


$\begin{matrix}H\\H\end{matrix}{>}N{-}O{-}Na$

Sodium hydroxylamate.
[Hydroxylamine an acid.]

The formation of oximes and hydroximic acids from hydroxylamine, and of, say, *ethylnitrolic acid*, $CH_3.C(NO_2)NOH$, from dibromonitroethane, $CH_3.CBr_2(NO_2)$, and hydroxylamine, observed by V. Meyer:


$$HO{-}N{<}\boxed{\begin{matrix}H\\H\end{matrix}+\begin{matrix}Br\\Br\end{matrix}}{>}C{<}\begin{matrix}CH_3\\NO_2\end{matrix}\rightarrow 2HBr+HO{-}N{=}C{<}\begin{matrix}CH_3\\NO_2\end{matrix}$$

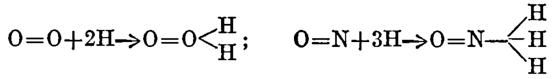
and the formation of *iso-diazobenzene*, $C_6H_5.N:NOH$, from nitrosobenzene, C_6H_5NO, and hydroxylamine, observed by E. Bamberger and E. Renauld:

$$C_6H_5{-}N{=}\boxed{O+H_2}{=}N{-}OH\rightarrow H_2O+C_6H_5{-}N{=}N{-}OH$$

favour the amido-formula, and these reactions all take place in alkaline solutions. In these cases, hydroxylamine is not an oxidizing agent in the sense of the reaction $H_3N{=}O\rightarrow NH_3+O$, but it appears to act in this way in acid solutions. For instance, hydroxylamine oxidizes a sulphuric acid soln. of vanadium sesquioxide to vanadic acid, and it exerts a similar action on the sesquioxides of titanium and molybdenum:

$$H_3N{=}\boxed{O+Ti_2O_3}\rightarrow NH_3+2TiO_2$$

According to S. M. Tanatar, also, sulphurous acid is oxidized to sulphuric acid by hydroxylamine hydrochloride, and the latter is at the same time reduced to ammonia: $H_2SO_3+NH_3O.HCl\rightarrow(NH_4)HSO_4+HCl$. Several organic compounds, too, are oxidized in an analogous manner. Just as hydrogen dioxide can be regarded as a reduction product of oxygen (1. 14, 13), so, in acid soln., hydroxylamine is formed as a reduction product of the nitric oxide



$$O{=}O+2H\rightarrow O{=}O{<}\begin{matrix}H\\H\end{matrix};\qquad O{=}N+3H\rightarrow O{=}N{-}{<}\begin{matrix}H\\H\\H\end{matrix}$$

and not as an oxidation product of ammonia or hydrazine.

Doubled formulæ like that of J. Donath $H_4{\equiv}N{=}O_2{=}N{\equiv}H_4$; and the imaginary anhydride $H_2{=}N{-}O{-}N{=}H_2$ of E. Divers were abandoned after C. A. Lobry de Bruyn had determined the mol. wt. of hydroxylamine to be 33.

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§ 24. The Salts of Hydroxylamine

The preparation of normal **hydroxylamine chloride,** $(NH_3OH)Cl$, or, as it is also represented, $NH_2OH.HCl$, *hydroxylamine hydrochloride* or *chlorohydrate*, has been indicated in connection with the preparation of hydroxylamine by the reducing action of hydrochloric acid and tin, or stannous chloride on nitric acid, or nitrites; and electrolytically. W. Lossen [1] also obtained it by the neutralization of the free base with hydrochloric acid. M. Adams obtained the salt by double decomposition between barium chloride and hydroxylamine sulphate. W. L. Semon used a modification of E. Divers' process in which the conversion of sodium carbonate, first into a mixture of hydrocarbonate and hydrosulphite, and then into hydrosulphite alone is carried out prior to the addition of the sodium nitrite, as a result of which the time required for the complete operation and the amount of cooling necessary are considerably reduced. Further, the sodium hydroxylaminedisulphonate is converted directly into acetoxime as recommended by F. Raschig, and this is then hydrolyzed by hydrochloric acid and the required hydroxylamine hydrochloride obtained after distilling off the acetone as indicated by A. Janny. Under these conditions, a product is obtained free from ammonium salts and with a yield of 53–77 per cent.—*vide supra*, hydroxylamine. It was also prepared by P. J. Eichkoff.

The salt occurs in thin plates by cooling the hot, sat., alcoholic soln.; in small crystals, by the slow evaporation of the soln.; and in plates, by the conc. of its aq. soln. The monoclinic prisms were found by V. von Lang to have the axial ratios $a:b:c=2{\cdot}0108:1:3028$, and $\beta=92°\ 57'$. The crystals show no crystallographic relations with those of ammonium chloride, although O. Lehmann said that the two salts crystallize in *regelmässiger Anlagerung.* H. Schiff and U. Monsacchi gave 1·676 for the sp. gr. at 17°/4°; and for the soln., they gave $D=1+0{\cdot}00425w+0{\cdot}0_595w^2$, where w denotes the percentage content of hydroxylamine chloride in the soln. During the dissolution, there is a contraction of —0·432 with soln. containing 40 per cent. of salt—sp. gr. 1·1852—an expansion of 0·192 with 20 per cent. soln.—sp. gr. 1·0888—and an expansion of 0·261 with 10 per cent. soln.—sp. gr. 1·0437. G. Tammann found the vap. press. of water by soln. with 10·48, 19·80, and 34·24 grms. of salt per 100 grms. of water to be depressed 34·2, 65·6, and 109·5 mm. respectively. W. Lossen said the salt does not lose weight when dried at 120° over conc. sulphuric acid; and it melts at about 151° with rapid decomposition, forming water, hydrogen chloride, ammonium chloride, nitrogen, and possibly nitrous oxide. P. J. Eichkoff said that it melts at 151° and decomposes at a higher temp.; W. H. Ross gave 157° for the m.p., and represented the decomposition: $3(NH_3OH)Cl=NH_4Cl+2HCl+N_2+3H_2O$. M. Berthelot gave $(2H_2,Cl,Nl,O)=70{\cdot}8$ Cals. for the heat of formation; and J. Thomsen, 18·5 Cals. for the heat of neutralization with hydrochloric acid. H. Remy measured the electrolytic transport of water in soln. of hydroxylamine hydrochloride. E. Ebler studied the mol. dispersion of aq. soln. of hydroxylamine hydrochloride. W. H. Ross gave for the electrical conductivity, μ, at 18°, in terms of mercury, with soln. of vol. v per mol of salt:

v . .	2	5	10	20	50	100	500	1000	5000	10,000
μ . .	73·3	80·5	86·6	90·9	95·8	98·9	101·5	107·6	111·6	112·4

E. Divers and T. Haga noted the gradual decomposition of the salt when it is impure. The salt readily dissolves in water and there is a marked fall of temp., and H. Schiff and U. Monsacchi said that at 17°, 100 parts of water dissolve 83·3 parts of salt, The dried salt is only sparingly soluble in absolute alcohol; and is precipitated from its soln. by ether. The hydrolysis of the aq. soln. observed by K. Winkelblech, and V. H. Veley has been discussed in connection with the base itself. The same remark applies to the actions of hydroxylamine hydrochloride on hydrogen dioxide, by C. Wurster; on alcoholic hypochlorites, by W. O. de Coninck; on the alkali nitrites, by S. M. Tanatar; on soln. of copper salts by G. von Knorre and K. Arndt, and E. Ebler; on acid soln. of ferric salts, by W. Meyeringh; and on the salts of silver, gold, cadmium, mercury, bismuth, tin, and arsenic, and on the molybdates, tungstates, and vanadates by E. Ebler. W. Lossen, and E. J. Maumené found nitric oxide and other gases are given off when the chloride is triturated with cupric oxide. Ammonium chloride was produced by the oxidation of crocionic acid by hydroxylamine chloride (R. Nietzki and T. Benckiser), of oxanthranol (E. von Meyer), and of triphenylvinylalcohol (H. Biltz). J. A. Muller found that the hydrochloric acid in hydroxylamine hydrochloride can be titrated with standard sodium hydroxide by using phenolphthalein as indicator provided carbon dioxide is absent. The free base does not act on that indicator.

By mixing a soln. of 42 grms. of hydroxylamine hydrochloride, in 48 c.c. of water, with a soln. of 20 grms. of hydroxylamine in 260 grms. of absolute alcohol; washing the precipitate with alcohol, then with ether, and finally drying in a current of air, W. Lossen obtained **hydroxylamine hemichloride,** $2NH_2OH.HCl$. It is also called basic hydroxylamine hydrochloride. He obtained the same product by adding ether to the mother-liquid obtained in preparing the normal chloride. The salt appears in rhombic prisms when a soln. in the smallest possible amount of hot water is cooled, or when the soln. is evaporated over conc. sulphuric acid. The crystals precipitated by alcohol are tabular. The salt melts at about 85° with the evolution of gas. The crystals are deliquescent in moist air; and they are slightly soluble in alcohol, but not in ether. The aq. soln. gives off hydroxylamine at ordinary temp. W. Lossen also reported hydroxylamine ditritachloride, $3NH_2OH.2HCl$, to be formed from a mixed soln. of the normal and the hemichloride. The rhombic crystals melt at about 95° with the evolution of gas. The hemichloride crystallizes from an aq. soln. of the ditritachloride. The deliquescent crystals are but sparingly soluble in alcohol, and insoluble in ether. W. R. Dunstan and E. Goulding stated that the evidence in favour of the existence of this product as a chemical individual is not free from objections.

M. Adams prepared normal **hydroxylamine bromide,** $NH_2OH.HBr$, by adding barium bromide to a soln. of hydroxylamine sulphate in excess. The filtered soln. was evaporated to dryness, and the residue extracted with absolute alcohol. The purified crystals are stable in the absence of air; the impure crystals become brown when exposed to light. The salt is readily soluble in water, and insoluble in ether. It is a stronger reducing agent than the chloride. It forms double salts with mercury and cadmium bromides. M. Adams prepared **hydroxylamine hemibromide,** $2NH_2OH.HBr$, or basic hydroxylamine bromohydrate, by adding hydroxylamine to a conc. alcoholic soln. of the normal salt; and by the action of the normal salt on mercuric oxide: $HgO+4(NH_2OH.HBr)=HgBr_2+H_2O+2(NH_2OH)_2HBr$. The white tabular crystals are readily soluble in water, but insoluble in ether or ligroïn.

R. Wolffenstein and F. Groll made normal **hydroxylamine iodide,** $NH_2OH.HI$, in colourless needles, by evaporating a soln. of eq. proportions of hydroxylamine and hydriodic acid, in vacuo, at 26°. The salt was also made by M. Adams, who said that the salt is very unstable, deliquescent in air, and furnishes a yellow soln. The instability, said W. R. Dunstan and E. Goulding, is due to the reducing action of hydrogen iodide on hydroxylamine. R. Wolffenstein and F. Groll recrystallized the salt from methyl alcohol. When warmed, iodine separates, and at 83°–84°, the salt decomposes with explosive violence. W. R. Dunstan and E. Goulding prepared

hydroxylamine hemiiodide, $2NH_2OH.HI$, by evaporating an alcoholic soln. of eq. proportions of hydroxylamine and methyl iodide or hydriodic acid, or by evaporating the mother-liquid obtained in the preparation of the tritaiodide; M. Adams obtained it from an ethereal soln. of the normal iodide. The tabular crystals are deliquescent; they are readily soluble in water, and in methyl or ethyl alcohol, but are not soluble in ether. When recrystallized from water, iodine is set free. The aq. soln. is acid, and is a strong reducing agent. The salt is best recrystallized from methyl alcohol, for then only a very small proportion of salt is decomposed. W. R. Dunstan and E. Goulding could not make the 3 : 2 salt: *hydroxylamine ditritaiodide;* but they obtained **hydroxylamine tritaiodide,** $3NH_2OH.HI$, by dissolving theoretical proportions of hydroxylamine and hydriodic acid in methyl alcohol, and fractionally precipitating the salts with ether so as to separate the normal and tritaiodides. O. Piloty and O. Ruff made the salt by the action of butyl iodide on hydroxylamine. W. R. Dunstan and E. Goulding said that the white tabular crystals are stable in dry air. O. Piloty and O. Ruff gave 103°–104° for the m.p. According to W. R. Dunstan and E. Goulding, at about 100°, the salt suddenly decomposes: $3NH_2OH.HI=NH_4I+N_2+3H_2O$; when recrystallized from hot methyl alcohol, or from water, there is a loss of hydroxylamine and the hemiiodide is formed; the tritaiodide is produced if an excess of hydroxylamine be always present. The aq. soln. has an acid reaction, and is a strong reducing agent.

W. Lossen prepared normal **hydroxylamine sulphate,** $(NH_2OH)_2H_2SO_4$, by evaporating a mixture of the normal chloride with the calculated quantity of sulphuric acid, and extracting the residue with alcohol. The methods of R. Preibisch, F. Raschig, E. Divers and T. Haga, J. Tafel, and C. F. Böhringer—indicated in connection with the preparation of hydroxylamine—can be employed. W. Lossen said that the cooling of the hot aq. soln. furnishes prismatic crystals, which, according to V. von Lang, belong to the monoclinic system, and, according to J. H. E. Dathe, to the triclinic system. W. Lossen found that the sulphate dried over conc. sulphuric acid does not lose in weight at 110°, and melts with decomposition at about 170°; S. S. Kolotoff found a loss in weight occurs between 125° and 130°, and added that the loss is rapid at 136°; and R. Preibisch gave 140° for the m.p. and the temp. of decomposition: $4(NH_2OH)_2H_2SO_4=4(NH_4)HSO_4+N_2+2NO+6H_2O$. W. H. Ross gave 163° for the m.p. and represented the accompanying decomposition; $3(NH_3.OH)_2SO_4=(NH_4)_2SO_4+2SO_2+2N_2O+8H_2O$. J. Thomsen, and M. Berthelot gave for the heat of formation, $(N_2,4H_2,S,3O_2)=280{\cdot}20$ Cals., for the heat of neutralization $(NH_2OH,\frac{1}{2}H_2SO_4)=10{\cdot}79$ Cals.; and for the heat of soln., —5'8 Cals. (M. Berthelot) or —9·6 Cals. (J. Thomsen). J. Tafel found that electrolytic reduction of hydroxylamine occurs at the copper cathode, only when the conc. of the sulphuric acid about the cathode falls below a certain critical value—*vide supra,* hydroxylamine. W. H. Ross gave for the electrical conductivity, μ, at 18° in terms of mercury with soln. containing a mol of salt in v vols.

v . .	5	10	20	50	100	500	1000	5000	10,000
μ . .	63·8	71·6	80·5	92·0	97·7	109·3	113·0	118·9	120·3

E. Divers and T. Haga said that the salt is not hygroscopic, but H. Schröder said that when triturated, the powder becomes moist owing to the decomposition brought about by the friction. The salt is soluble in water; E. Divers and T. Haga said that 133 parts of salt dissolve in 100 parts of water. M. Adams found that 100 grms. of water dissolve S grm. of salt:

	−8°	0°	10°	20°	30°	40°	50°	60°	90°
S . .	30·7	32·9	36·6	41·3	44·1	48·2	52·2	56·0	68·5

R. Preibisch found the salt to be insoluble in alcohol and ether, and M. Adams said that when dry, the salt is insoluble in absolute alcohol and almost insoluble in 95 per cent. alcohol. W. Lossen found that alcohol precipitates the salt in needles from its conc. aq. soln. The aq. soln. has an acid reaction, but R. Preibisch found that it would not drive carbon dioxide completely from the carbonates in the cold. The reactions indicated in connection with hydroxylamine were often produced by the sulphate. The reducing action on the iodates, bromates, and chlorates was discussed by D. Vitali, M. Schlötter, and P. Jannasch and A. Jahn. Similarly, C. Wurster discussed the oxidizing action of hydrogen dioxide. According to R. Preibisch, the crystals dissolve in conc. sulphuric acid without developing any gas. J. Tafel said that the sulphate is so stable in 50 per cent. sulphuric acid, that the soln. can be warmed to 40° without decomposition. A. Angeli and F. Angelico studied the decomposition of hydroxylamine sulphate by persulphates. R. Preibisch found a copious evolution of gas when hydroxylamine dissolves in conc. nitric acid. J. Tafel found that a soln. of hydroxylamine sulphate in 50 per cent. sulphuric acid is not changed in the cold by the addition of 50 per cent. nitric acid; a soln. of 0·64 grm. of hydroxylamine sulphate, 0·65 grm. nitric acid, and 10 c.c. of 50 per cent. sulphuric acid is not changed by keeping 7 hrs. at 15°; when warmed to 41°–42°, much gas is given off; if 40 per cent. sulphuric acid is used, decomposition occurs at 24°–27°; with 30 per cent. sulphuric acid, decomposition begins at 100° with explosive violence. V. Meyer, and W. Wislicenus discussed the action of nitrous acid or nitrites—*vide* hydroxylamine. R. Preibisch found hydroxylamine sulphate is not perceptibly altered by conc. aq. ammonia; but it dissolves in soda-lye, and the soln. smells of ammonia. J. Tafel found that a soln. of hydroxylamine sulphate in 50 per cent. sulphuric acid is quite stable in the presence of powdered copper sulphate or metallic copper. R. Preibisch said that silver nitrate produces a white precipitate and when ammonia is added much gas is evolved, and silver is deposited. Gas is vigorously evolved when the aq. soln. of hydroxylamine sulphate is treated with potassium dichromate —the gas contains nitrogen and nitric oxide in the ratio 1 : 2. A similar evolution of gas occurs with manganese dioxide and sulphuric acid. These reactions were also studied by G. Bertoni. Complex salts with the metal sulphates were studied by W. Meyeringh, M. Adams, and E. Knövenagel and E. Ebler.

J. Tafel believed that the soln. of hydroxylamine sulphate in 50 per cent. sulphuric acid contained a salt $NH_2OH.H_2SO_4$, **hydroxylamine hydrosulphate.** A. Lidoff obtained this salt by the action of hydrosulphurous acid on potassium nitrite; and E. Divers, by digesting the normal chloride with the calculated quantity of sulphuric acid, and evaporating in cold air. The prismatic crystals are very deliquescent.

According to V. Meyer, no *hydroxylamine carbonate* has been produced; but H. Goldschmidt and K. L. Syngros prepared complex carbonates with zinc, manganese, iron, and nickel salts. W. Lossen treated hydroxylamine chloride with silver nitrate or hydroxylamine sulphate with barium nitrate, and on evaporating the filtered soln. obtained an oily liquid, which M. Berthelot and G. André cooled to —10°, and obtained a white, hygroscopic mass of **hydroxylamine nitrate,** $NH_2OH.HNO_3$. W. H. Ross could prepare only a viscid colourless liquid which he obtained by distilling the aq. soln. at 20 mm. press., and drying over phosphoric oxide. The salt melts at 48°, and decomposes at 100°, forming nitrogen, water, and oxygen. The heat of soln. is —5·9 Cals., the heat of neutralization, 9·2 Cals.; and the reaction $NH_2OH.HNO_3=N_2+O_2+2H_2O$ develops 51·4 Cals. at constant vol., or 50·3 Cals. at constant press. Hence the heat of formation is (N,3H,O) =86·4 Cals. W. H. Ross found the electrical conductivity, μ, at 18° on terms of mercury for soln. with a mol salt of in v vols., to be:

v .	5	10	20	50	100	500	1000	5000	10,000
μ .	—	106·7	112·6	119·1	122·8	127·1	129·9	134·0	135·5

The nitrate has a greater conductivity than the chloride which would not be expected from the behaviour of the corresponding salts of the alkalies. L. J. Simon represented the reaction with potassium permanganate by $2KMnO_4+5(NH_2OH.HNO_3)$ $=2Mn(NO_3)_2+2KNO_2+2N_2O+10H_2O$. W. Lossen reported normal **hydroxylamine orthophosphate,** $(NH_2OH)_3.H_3PO_4$, to be formed by mixing aq. soln.

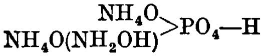
of hydroxylamine chloride or sulphate and disodium hydrophosphate; and V. Kohlschütter and K. A. Hofmann, by mixing barium hydrophosphate and hydroxylamine sulphate, and adding alcohol to the filtered liquid; metaphosphoric acid neutralized with ammonia and mixed with hydroxylamine chloride furnishes this same salt. W. Lossen obtained small crystals which give only a syrupy mass when the aq. soln. is evaporated. W. H. Ross found that when the salt is heated in vacuo its decomposition is represented by $2(NH_2OH)_3.H_3PO_4 = 6NH_2OH + H_2O + H_4P_2O_7$. The electrical conductivity, μ, at 18° in terms of mercury for soln. with mol a of the salt in v vols. is as follows:

v	5	10	20	50	100	500	1000	5000	10,000
μ	19·8	22·0	23·6	24·7	25·5	26·4	26·6	27·0	27·1

The salt is only sparingly soluble in water, and according, to W. H. Ross, readily forms supersaturated soln. According to M. Adams, 100 grms. of water dissolve S grm. of salt:

	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°
S	1·2	1·5	1·9	2·8	4·0	5·5	7·7	10·2	13·3	16·8

The hot aq. soln. reacts feebly acid. Dry ammonia gas liberates hydroxylamine, forming ammonium phosphate. The analogous ammonium salt, $(NH_3)_3.H_3PO_4$, is difficult to prepare, and the hydroxylamine salt may be constituted:



$$\begin{matrix} NH_4O \\ NH_4O(NH_2OH) \end{matrix} > PO_4{-}H$$

L. J. Simon represented the reaction with potassium permanganate $12KMnO_4 + 16\{(NH_2OH)_3H_3PO_4\} = 4Mn_3(PO_4)_2 + 6KH_2PO_4 + 2K_2HPO_4 + 2KNO_2 + 20N_2 + 3N_2O + 89H_2O$. A. P. Sabanéeff obtained **hydroxylamine dihydrophosphate,** $2NH_2OH.H_3PO_4$, or $(NH_3OH)_2HPO_4$, from monohydroxylamine phosphate by treatment with alcohol.

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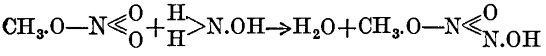
§ 25. Nitrohydroxylaminic Acid

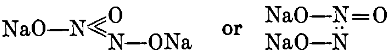
If a soln. of hydroxylamine and sodium hydroxide in methyl alcohol be treated with methyl nitrate, a white powder is precipitated; it appears to be the sodium salt of an unstable acid—**nitrohydroxylaminic acid,** $H_2N_2O_3$—and it has the empirical formula $Na_2N_2O_3$. A. Angeli [1] has prepared a whole series of similar salts—*e.g.* potassium, alkaline earths, lead, cadmium, and cerium nitrohydroxylaminates—and also some inorganic esters—*e.g.* $H(C_2H_5)N_2O_3$; $H(C_6H_5)N_2O_3$; etc. The reaction between methyl nitrate, $CH_3.NO_3$, and hydroxylamine probably progresses:



$$CH_3.O—N{<}\begin{matrix}O\\O\end{matrix}+\begin{matrix}H\\H\end{matrix}{>}N.OH\rightarrow H_2O+CH_3.O—N{<}\begin{matrix}O\\N.OH\end{matrix}$$

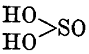
Methyl nitrate. Methyl nitrohydroxylaminate.

and **sodium nitrohydroxylaminate,** NaO.NO : N.ONa, is formed by the displacement of the methyl group and hydrogen by sodium. The various reactions of the sodium salt agree with the structural formula:



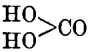
$$NaO—N{<}\begin{matrix}O\\N—ONa\end{matrix}\quad\text{or}\quad\begin{matrix}NaO—N=O\\NaO—\ddot{N}\end{matrix}$$

If the sodium salt be treated with a mineral acid, there is a brisk effervescence, and nitric oxide is evolved $H_2N_2O_3\rightarrow 2NO+H_2O$, hence the compound has been regarded as a *hydrate of nitric oxide.* In this respect, nitrohydroxylaminic acid is brought into line with sulphurous and carbonic acids, both of which give the corresponding anhydrides when their salts are treated with acids:



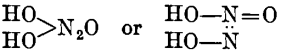
$$\begin{matrix}HO\\HO\end{matrix}{>}SO$$

Sulphurous acid.



$$\begin{matrix}HO\\HO\end{matrix}{>}CO$$

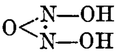
Carbonic acid.



$$\begin{matrix}HO\\HO\end{matrix}{>}N_2O\quad\text{or}\quad\begin{matrix}HO—N=O\\HO—\ddot{N}\end{matrix}$$

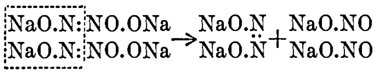
Nitrohydroxylaminic acid.

Four years earlier than A. Angeli, A. Thum had found evidence of the existence of what he called *azoxyhydroxyl:*



$$O{<}\begin{matrix}\dot{N}—OH\\\dot{N}—OH\end{matrix}$$

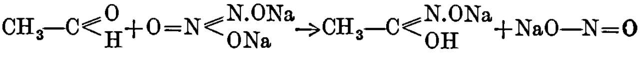
but was unable to isolate it. A. Angeli and co-workers found that when sodium nitrohydroxylaminate is exposed to air, oxygen is rapidly absorbed, and a mixture of sodium nitrite and nitrate is formed. If a soln. of the sodium salt be allowed to stand in the cold, nitrous acid is slowly evolved; and if boiled, half the total nitrogen in the salt forms nitrous oxide, and half sodium nitrite: $2(NaO.N:NO.ONa)+H_2O\rightarrow N_2O+2NaNO_2+2NaOH$. When the sodium salt is warmed, it melts to a greenish liquid, forming a mixture of sodium nitrite and hyponitrite:



$$\begin{matrix}NaO.N:\\NaO.N:\end{matrix}\begin{matrix}NO.ONa\\NO.ONa\end{matrix}\rightarrow\begin{matrix}NaO.\ddot{N}\\NaO.\ddot{N}\end{matrix}+\begin{matrix}NaO.NO\\NaO.NO\end{matrix}$$

and the nitrous oxide formed in the previous reaction may be derived from sodium hyponitrite formed as an intermediate product of the decomposition. A. Angeli and F. Angelico prepared **potassium nitrohydroxylaminate,** $K_2N_2O_3$. F. Angelico and S. Fanara could not prepare *ammonium nitrohydroxylaminate,* or *hydrazine nitrohydroxylaminate.* When the sodium salt is treated with silver nitrate, yellowish **silver nitrohydroxylaminate,** AgO.N : NO.OAg, is formed, but being very unstable, it immediately breaks down into silver, nitric oxide, and silver nitrite: $AgO.N:NO.OAg\rightarrow Ag+NO+AgNO_2$. A. Angeli and G. Marchetti think that silver hyponitrite is formed as an intermediate product. The silver salt can be kept at a temp. below 0° for some time without decomposition. A. Angeli and F. Angelico, and F. Angelico and S. Fanara obtained **calcium nitrohydroxylaminate,** $CaN_2O_3.3\tfrac{1}{2}H_2O$;

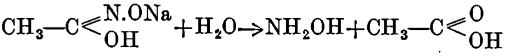
strontium nitrohydroxylaminate, $SrN_2O_3.1\frac{1}{2}H_2O$; and **barium nitrohydroxylaminate,** $BaN_2O_3.H_2O$. F. Angelico and S. Fanara prepared **cadmium nitrohydroxylaminate,** $CdN_2O_3.H_2O$, by mixing equimolar quantities of the sodium salt and crystalline cadmium sulphate. It resembles the barium salt. It begins to decompose at 110°, and is completely decomposed at 200°. The salt becomes anhydrous at 100°. A. Angeli and F. Angelico prepared a basic **cerium nitrohydroxylaminate,** $Ce_2(N_2O_3)_3.Ce(OH)_3$; and **lead nitrohydroxylaminate,** PbN_2O_3. Again, when sodium nitroxylaminate is allowed to react with an aldehyde, say acetaldehyde, $CH_3.COH$, a sodium salt of **acetohydroximic acid** is formed:



$$CH_3{-}C{<}{}^{O}_{H}+O{=}N{<}{}^{N.ONa}_{ONa}\rightarrow CH_3{-}C{<}{}^{N.ONa}_{OH}+NaO{-}N{=}O$$

Acetaldehyde. Acetohydroximic acid.

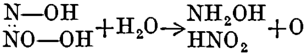
The relative proportions of the two end-products show that the generalized reaction, so to speak, can be written $HO.N:NO.O\rightarrow HNO_2+NO$. The salt of acetohydroximic acid so obtained is hydrolyzed by boiling with acids, and hydroxylamine and an organic acid (acetic acid, $CH_3.CO.OH$) are formed:



$$CH_3{-}C{<}{}^{N.ONa}_{OH}+H_2O\rightarrow NH_2OH+CH_3{-}C{<}{}^{O}_{OH}$$

Acethoydroximic acid. Acetic acid.

The resultant effect, the end-products of the action of nitrohydroxylaminic acid on aldehyde can be generalized, so to speak, in a symbolic form by the equation:



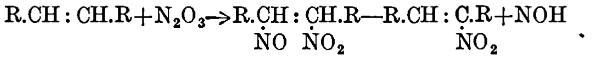
$$\begin{matrix}N{-}OH\\ \ddot{N}O{-}OH\end{matrix}+H_2O\rightarrow\begin{matrix}NH_2OH\\ HNO_2\end{matrix}+O$$

for the oxygen atom has transformed the aldehyde group CO.H into the acid group CO.OH. These reactions are particularly interesting, for they show that the acid and its salts can decompose in at least six different ways which A. Angeli and F. Angelico summarize:

(1)	$2H_2N_2O_3=$	$4NO+2H_2O$	Free acid.
(2)		$2HNO_2+2NO+H_2$	Silver salt.
(3)		$2HNO_2+2NOH$	Sodium salt.
(4)		$2HNO_2+N_2O+H_2O$	Sodium salt.
(5)		$2HNO_2+H_2N_2O_2$	Sodium salt.
(6)	$+2H_2O$	$2HNO_2+2NH_2OH+O_2$	*Via* hydroximic acid.

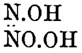
Nitroyl, NOH.—A. Angeli in his extensive studies, *Ueber einige sauerstoffhaltige Verbindungen des Stickstoffs* (Stuttgart, 1908), found it convenient to call the group NOH, *nitrosyl*, a rather unfortunate term because the same word has long been used for the monad radicle NO; consequently, the term *nitrotyl*, or *nitroyl*, has been recommended in place of A. Angeli's nitrosyl. This group can act as a dyad radicle, forming with the aldehydes, R.COH, a **hydroximinic acid,** $R(OH)C{=}NOH$ (*vide supra*), which recalls the union of oxygen with an aldehyde to form an acid—*e.g.* acetaldehyde, $CH_3.COH$, unites with an atom of oxygen to form acetic acid, $CH_3.CO.OH$; hyponitrous acid is regarded as *dinitroyl*, HON : NOH, recalling the formation of a mol. of oxygen O : O, by the union of two oxygen atoms. Nitroyl is considered to be the anhydride of dihydroxyammonia: $NH(OH)_2\rightarrow H_2O+NOH$. A. Angeli considers *the formation of hydroximic acid by reaction with an aldehyde indicates the presence of the nitroyl group.* In virtue of this reaction, nitrohydroxylaminic acid is itself supposed to contain a nitroyl group. Neither dihydroxyammonia nor nitroyl has been isolated, but their presence has been inferred in the products of certain reactions. A. Kurtenacker and R. Neusser said that nitrogen is produced by the interaction of hydroxylamine with nitroyl.

When certain unsaturated carbon compounds—*e.g.* isosafrol, R.CH : CH.R—are treated with nitrous acid, they take up additively N_2O_3 to form the so-called *isonitrites*, and the isonitrites when treated with alkalies yield a soln. containing a nitro-derivative and nitroyl. In symbols:



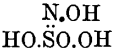
$$R.CH:CH.R+N_2O_3\rightarrow R.\underset{NO}{CH}:\underset{NO_2}{CH}.R—R.CH:\underset{NO_2}{C}.R+NOH$$

A. Angeli found hyponitrous acid in the soln. containing the end-products of the reaction, and the soln. also gave the nitroyl reaction, and he also found that the products of the saponification of *potassium hydroxylamine sulphonate* gave reactions indicating the presence of sulphites, hyponitrites, and nitroyl; he represented the compound in question by $HO.N:SO(OK)_2$ in preference to E. Divers and T. Haga's formula $H(OH)N.SO.OH$; and he represented its decomposition by the equation $HO.N:SO(OK)_2\rightarrow NOH+SO(OK)_2$. Similar remarks apply to *benzene sulphohydroximic acid*, which O. Piloty symbolized $C_6H_5.SO_2.NH.OH$, but which A. Angeli prefers to represent $HO.N:SO(OH)C_6H_5$, because it, too, when hydrolyzed by an alkali gives the nitroyl reaction. The analogy in the constitution of these three substances is inferred from the similarity in their behaviour, and the presence of the nitroyl group in each is represented by the analogous formulæ:



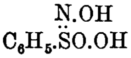
$$\begin{matrix}N.OH\\ \ddot{N}O.OH\end{matrix}$$

Nitrohydroxylamine acid.



$$\begin{matrix}N.OH\\ HO.\ddot{S}O.OH\end{matrix}$$

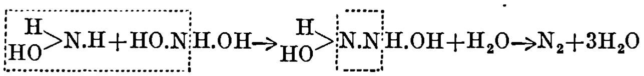
Hydroxylamine sulphonic acid.



$$\begin{matrix}N.OH\\ C_6H_5.\ddot{S}O.OH\end{matrix}$$

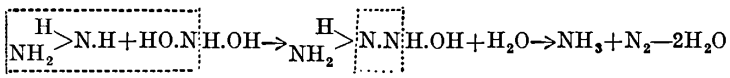
Benzene sulphohydroximic acid.

A. Angeli considers that in aq. soln. nitroyl probably exists as **nitroyl hydrate,** $NOH.H_2O$, which is isomeric, at any rate, with **dihydroxyammonia,** $(HO)_2NH$, and he further emphasizes the properties of nitroyl by showing that (i) it reacts with the alkyl iodides, forming oximes—characterized by the dyad group C : NOH—the same as are produced by the action of hydroxylamine on aldehydes. The oximes give hydroxylamine when hydrolyzed with acids; (ii) with nitrobenzene, $C_6H_5.NO$, it gives the same product $C_6H_5—NO{=}NOH$ as is obtained by the action of hydroxylamine on nitrobenzene; (iii) with hydroxylamine there is an evolution of nitrogen and formation of water:



$$\boxed{{}^{H}_{HO}{>}N.H+HO.N}H.OH\rightarrow {}^{H}_{HO}{>}\boxed{N.N}H.OH+H_2O\rightarrow N_2+3H_2O$$

and (iv) with hydrazine, $H_2N.NH_2$, it forms ammonia, nitrogen, and water:



$$\boxed{{}^{H}_{NH_2}{>}N.H+HO.N}H.OH\rightarrow {}^{H}_{NH_2}{>}\boxed{N.N}H.OH+H_2O\rightarrow NH_3+N_2—2H_2O$$

Summarizing the hydroxyl derivatives of ammonia, it will be seen that the introduction of hydroxyl increase the acidity and diminishes the stability of the resulting compounds:

TABLE XXVIII.—HYDROXYL DERIVATIVES OF AMMONIA.

—	NH_3 Ammonia.	NH_2OH Hydroxylamine.	$NH(OH)_2$ Dihydroxyammonia or nitroyl hydrate.	$N(OH)_3$ Ortho-nitrous acid.
Basicity . . .	Weak base	Weaker base	[Neutral ?]	Weak acid
Stability . . .	Stable	Unstable	Not isolated	Not isolated
With aldehydes .	Addition compd.	Oximes	Oximes	Nitrous acid nil
With ketones . .	—	Oximes	Nil	Reacts

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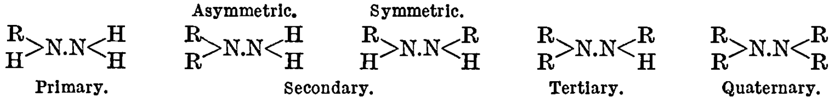
§ 26. Hydrazine or Diamide

The name **hydrazine** was applied by E. Fischer[1] in 1875 to the then hypothetical **diamide,** a kind of doubled ammonia, $H_2{=}N{-}N{=}H_2$, which he foresaw must be the parent of a series of substitution products in which the hydrocarbon radicles take the place of the hydrogen atoms. Twelve years earlier, A. W. Hofmann discovered the disubstituted symmetrical $(C_6H_5)H{=}N{-}N{=}H(C_6H_5)$, which he called **hydrazobenzene**; and in 1875, E. Fischer made the monosubstituted derivative, $(C_6H_5)H{=}N{-}N{=}H_2$, which he called **phenylhydrazine,** by treating aniline, $C_6H_5NH_2$, with nitrous acid so as to form **diazobenzene,** $C_6H_5N:N.OH$; and reducing the diazobenzene with stannous chloride and hydrochloric acid, so as to form the phenylhydrazine.

The four hydrogen atoms of the parent $H_2N.NH_2$ can be replaced by hydrocarbon radicles, R, in five different ways:

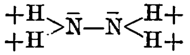


$$\begin{matrix}R\\H\end{matrix}\!>\!N.N\!<\!\begin{matrix}H\\H\end{matrix}\qquad\begin{matrix}R\\R\end{matrix}\!>\!N.N\!<\!\begin{matrix}H\\H\end{matrix}\qquad\begin{matrix}R\\H\end{matrix}\!>\!N.N\!<\!\begin{matrix}R\\H\end{matrix}\qquad\begin{matrix}R\\R\end{matrix}\!>\!N.N\!<\!\begin{matrix}R\\H\end{matrix}\qquad\begin{matrix}R\\R\end{matrix}\!>\!N.N\!<\!\begin{matrix}R\\R\end{matrix}$$

Asymmetric. Symmetric.

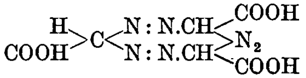
Primary. Secondary. Tertiary. Quaternary.

Representatives of all the five classes have been prepared, and the term hydrazine can be applied to all. H. Henstock gave for the electronic structure:



$$\begin{matrix}+H\\+H\end{matrix}\!>\!\bar{N}-\bar{N}\!<\!\begin{matrix}H+\\H+\end{matrix}$$

A. W. Hofmann's hydrazobenzene is symmetrical secondary hydrazine, or symmetrical diphenylhydrazine; and E. Fischer's phenylhydrazine is a primary compound. J. W. E. Glattfeld and C. H. Milligan made optically active hydrazines, *e.g.* dimethylpropylphenylhydrazine. The parent hydrazine was isolated in 1887, by T. Curtius, in the form of a hydrate and salts, by hydrolyzing **triazoacetic acid:**



$$\begin{matrix}H\\COOH\end{matrix}\!>\!C\!<\!\begin{matrix}N:N.CH\\N:N.CH\end{matrix}\!\begin{matrix}<COOH\\>N_2\\<COOH\end{matrix}$$

a compound, it will be observed, which contains the group —N : N— three times. Hydrazine has since been prepared from many other organic compounds containing paired nitrogen atoms; for instance, T. Curtius and R. Jay made it by the hydrolysis of amidoparaldimine, $C_6H_{12}O_2(N.NH_2)$; J. Thiele, by the hydrolysis of amidoguanidine, $NH_2.C(NH).NH.NH_2$; F. D. Chattaway, by the hydrolysis of paraurazide, $CO{=}(NH.NH)_2{=}CO$; W. Traube, by reducing methylenediisonitramine, $CH_2(N_2O_2)_2H_2$, with sodium amalgam; H. von Pechmann and P. Manck, by the hydrolysis of potassium sulphohydrazinomethylene disulphonate, $C(SO_3K)_2(NK)N.SO_3K.H_2O$; E. Buchner, by the hydrolysis of methyl furmaricdiazoacetate, $\{CH(COOCH_3)N\}_2CH.COOCH_3$, or ethyl cinnamicdiazoacetate, $(CHC_6H_5.N)\text{-}\{CH(COOH).N\}CH.COOC_2H_5$; and P. J. Schestakoff, by the action of sodium hypochlorite on urea: $NH_2.CO.NH_2+NaOCl=NH_2.C(ONa):NCl+H_2O$; followed by $NH_2.C(ONa):NCl=NH_2.N:CCl.ONa$; $NH_2.N:CCl.ONa+NaOH=NaCl+NH_2.NH.COONa$; and $NH_2.NH.COONa+H_2O=NaHCO_3+NH_2.NH_2$. F. Raschig said that a trace of hydrazine is formed in the oxidation of ammonia (*q.v.*). N. Tarugi said that in urine there is an oxydase which can split urca into carbon dioxide and hydrazine. The subject is discussed from the point of view of organic chemistry by N. V. Sidgwick, *The Organic Chemistry of Nitrogen* (Oxford, 1910); L. Spiegel, *Der Stickstoff und seine wichtigsten Verbindungen* (Braunschweig, 1902); H. Wieland, *Die Hydrazine* (Stuttgart, 1913); and H. Imbert, *De l'hydrazine et ses dérives* (Paris, 1899). The discovery and development of the different methods for preparing $NH_2.NH_2$ by organic chemists is an historical accident, for it can be prepared more simply from inorganic materials. H. S. Hirst, and W. A. Noyes detected traces of hydrazine and ammonia in the products of the action of nitrogen on hydrogen when exposed in silica tubes to ultra-violet light.

Hydrazine is a direct reduction product of hyponitrous acid. The presence of a sulphite is usually necessary for the reduction. Hydrazine does not usually appear as an intermediate stage in the formation of ammonia from nitric acid because, as shown by N. R. Dhar, it is more readily oxidized than ammonia by nitrous acid. P. Duden treated an alkaline soln. of potassium sulphite with nitrous oxide, and reduced the resulting potassium nitrosylsulphonate, $KSO_3.M(OK).NO$, with sodium amalgam in a conc. alkaline soln., at about 0°, in the presence of potassium hyponitrite and sulphite. The product is potassium hydrazine sulphite, $KSO_3.NH.NH_2$; formed by the reaction $KSO_3.N(KO).NO+3H_2 \rightarrow H_2O+KOH+KSO_3.NH.NH_2$. By acidifying and then warming the soln., hydrazine is set free. F. von Brackel obtained a very small yield of hydrazine by treating a soln. of hyponitrous acid with sodium hydrosulphite, evaporating the product in vacuo, and reducing it with zinc-dust and acetic acid. W. R. Hodgkinson and C. C. Trench also obtained a small yield by passing dry ammonia over heated and dry cupric sulphate. F. Raschig showed that a trace of hydrazine is formed in the limited oxidation of ammonia by oxygen: $4NH_3+O_2=2H_2O+2N_2H_4$; E. Divers and T. Haga, by the action of sodium amalgam on potassium nitrososulphate. A. Findlay noted the high tension brush discharge passing through a mixture of nitrogen and ammonia produces a little hydrazine. J. W. Turrentine and J. M. Olin found that the electrolysis of ammonium hydroxide in the presence of sodium chloride and glue, with a low current density furnishes hydrazine if the sodium chloride be added gradually in small quantities at a time during the electrolysis.

In 1907, F. Rashig showed that it is possible to make ammonia double itself, so to speak, by converting one part into chloramine, NH_2Cl, and bringing this into contact with more ammonia. The reaction is symbolized: $NH_3+NH_2Cl \rightarrow NH_2.NH_2.HCl$. This constructive reaction is opposed by the destructive changes $2NH_3+3NH_2Cl \rightarrow 3NH_4Cl+N_2$; and $2NH_2Cl+N_2H_4=2NH_4Cl+N_2$, which are favoured by decreasing the viscosity of the soln., say, by the addition of acetone, and it is retarded by the addition of substances, like glue or gelatin, which increase the viscosity of the soln. Hence, although the action of the glue or gelatin is not understood, the yield is much reduced if the colloid be absent. The reaction was studied by A. Stock.

Mix 200 c.c. of a 20 per cent. soln. of ammonia, 5 c.c. of a one per cent. soln. of glue or gelatine, and 100 c.c. of an aq. soln. of 7·5 grms. of sodium hypochlorite, free from an excess of chlorine—in a litre flask. Boil the mixture for about half an hour, when it will have evaporated to about half its original volume. Monochloramide is first formed, and this reacts with another mol. of ammonia to form hydrazine hydrochloride: $NH_2Cl+NH_3=N_2H_4.HCl$. When cold, place the flask in iced water, and add 20 c.c. of a soln. containing 1·96 grms. of sulphuric acid, H_2SO_4. Hydrazine sulphate crystallizes out. This may be purified by recrystallization from water. The process is used technically for the preparation of hydrazine sulphate.

N. Putochin, and B. P. Orelkin and co-workers used F. Raschig's method. R. A. Joyner studied the relation between the yield of hydrazine and the mol. ratio of ammonia to sodium hypochlorite and found the yield to be 5·7 per cent. when the ratio was 2·02; 32 per cent. with the ratio 8·8; and 75 per cent. with the ratio 76·8. With 0·400 mol of NH_3, 0·0100 mol of NaOCl in 110 c.c. of soln. and 0 mgrm. of gelatin, the yield was 2·0 per cent. of hydrazine; with 4·9 mgrms. of gelatin, the yield was 30·8 per cent.; and with 100·9 mgrms. of gelatin, the yield was 51 per cent. He found the yield was lowered by the addition of ammonium salts; it was scarcely affected by sodium sulphate or hydroxide, and was raised slightly by potassium chloride. The presence of hydrazine lowered the yield, showing that the opposing reaction is probably $2NH_2Cl+N_2H_4=2NH_4Cl+N_2$. Additions of gelatin, glue, and peptone had the same effect in raising the yield; starch, dextrine, and sucrose favoured the production of hydrazine, but only when present in amounts 100–300 times greater than that of gelatin. The effect of the sodium salts of glutamic acid, tyrosine, tryptophan, and uric acid was insignificant. Peptized silicic and stannic acids had strong catalyzing actions, the yield of hydrazine obtained with stannic acid being about equal to that produced by one-third the quantity of gelatin; with silicic acid, however, a yield equal to that obtained with glue could not be attained. The reaction was catalyzed by animal charcoal, wood charcoal, asbestos powder, and powdered meerschaum, when these were present in relatively large quantities. Kieselguhr, calcium phosphate, silica gel, French chalk, and kaolin had no action. There is no evidence of the formation of intermediate compounds between gelatin and chloroamine; and the acceleration of the reaction by glue may be due to a strong adsorption of the ammonia by the particles of glue, favouring the reaction $NH_2Cl+NH_3=N_2H_4.HCl$, and this also explains the favourable action of charcoal known to adsorb ammonia with avidity.

T. Curtius and H. Schulz prepared **hydrazine hydrate**, by distilling a mixture of hydrazine sulphate (100 grms.), potassium hydroxide (100 grms.), and water (250 grms.) in a silver retort provided with a silver condensing tube. The distillation was continued (5–6 hours) until the last drop had passed over, and the distillate (250 c.c.) was then fractionated, the fractions being best divided into below 101°, 101° to 104°, 104° to 117°, and 117° to the constant boiling temp. After four fractionations, the hydrazine hydrate (36 grms.) boiled constantly at 119°. C. A. Lobry de Bruyn avoided the use of the costly silver apparatus; he made the hydrate from commercial hydrazine sulphate by converting it into bromide by means of barium bromide, and this was then decomposed by the theoretical amount of aq. potash-lye. After the potassium bromide thus formed had been precipitated with alcohol, the alcoholic soln. of the hydrate was distilled under the ordinary press. until the temp. reached 108°, but little of the hydrate passing over below this point. Any further precipitate of potassium bromide having been removed, the liquid is fractionated first under atm. press. until the temp. reached 118°, and then under a press. of 121–125 mm., the fraction boiling at 73° contained 99·7 per cent. of hydrazine hydrate, and was free from silica. The yield, however, was only 22 per cent. of that required by theory. The barium salt can be dispensed with, and simple fractionation employed.

C. A. Lobry de Bruyn obtained nearly pure **anhydrous hydrazine** as a viscous liquid by distilling, under reduced press., a mixture of hydrazine hydrate and barium oxide prepared in a flask cooled by a freezing mixture. He obtained 92 per cent. hydrazine by boiling the hydrochloride with sodium methoxide for half an hour, $N_2H_4.HCl+NaOCH_3 \rightarrow NaCl+CH_3OH+N_2H_4$. After removing the sodium chloride, the liquid was distilled under reduced press. The first distillation gave 73 per cent. hydrazine; the second, 82–84 per cent.; and this after fractional crystallization gave a product with 92 per cent. hydrazine. Contact with rubber must be avoided. The product can be preserved in sealed glass tubes from which air has been displaced by hydrogen. C. F. Hale and F. F. Shetterly have studied the preparation of anhydrous hydrazine with barium oxide, barium hydroxide, and sodium hydroxide as dehydrating agents. Barium oxide gave the best results. E. Ebler and R. L. Krause also used barium oxide. A. Stähler used calcium oxide, and F. Raschig, sodium hydroxide. R. Stollé and K. Hofmann distilled hydrazine carboxylic acid, $NH_2.NHCOOH$, over calcium or barium oxide; A. Djawachoff heated hydrazine borate, $(N_2H_4)_2(B_2O_3)_6$, to 270° and obtained anhydrous hydrazine; and R. Stollé treated sodium amide with an excess of hydrazine hydrate: $N_2H_4.H_2O+NaNH_2=N_2H_4+NH_3+NaOH$. If the sodium amide be in excess the reaction was symbolized: $N_2H_4+NaNH_2=NH_3+NaN_2H_3$. T. Curtius and

F. Schrader said that pure hydrazine can be preserved in a sealed tube without alteration, but the dil. soln. rapidly loses its characteristic properties.

The physical properties of hydrazine and its hydrate.—Anhydrous hydrazine is a colourless, corrosive liquid which fumes strongly in air, and hydrazine hydrate may be described in the very same words. C. A. Lobry de Bruyn gave 1·014 for the sp. gr. of the hydrazine at 15°/15°, and 1·008 at 23°/15°; while J. W. Brühl gave 1·0256 at 0·2°/4°, and 1·0258 at 0°/4°. T. Curtius and H. Schulz gave 1·03 to 1·0305 for the sp. gr. of hydrazine hydrate at 21°. J. W. Dito found 1·0114 for the sp. gr. of hydrazine at 15°/4°, and as water is added, the sp. gr. rises to a maximum 1·0470 with 64·1 per cent. N_2H_4 corresponding with $N_2H_4.H_2O$; and with more water, the sp. gr. falls continuously. K. Jablczynsky measured the vol. of hydrazine ions. T. Curtius and H. Schulz found the vap. density of the hydrate at 100° in vacuo corresponded with the formula $N_2H_4.H_2O$; at 170°, with the complete dissociation $N_2H_4.H_2O \rightleftharpoons N_2H_4+H_2O$; and above 170°, the hydrazine breaks down. According to A. Scott, at 98·8°, the vap. density is 15·8 corresponding with $N_2H_4.H_2O$; the dissociation of the hydrate is complete, and above that temp. ammonia and nitrogen are formed. A. P. Sabanéeff found that some hydrazoic acid is formed when the hydrazine nitrates are decomposed by heat; and J. W. Turrentine showed that azoimide is produced by the decomposition of hydrazine nitrate and dinitrate. The decomposition of some other hydrazine salts has now been studied. F. Balla found practically all the current was consumed in the oxidation $N_2H_4+O_2=N_2+2H_2O$. C. A. Lobry de Bruyn found the b.p. of hydrazine to be 56° at 71 mm.; 113·5° at 761·5 mm.; and 134·6° at 1490 mm.; while the hydrate boils at 46° at 26 mm., and at 118·5° at 739·5 mm. The critical temp. of hydrazine is 380°, and the critical press., 145 atm. Hydrazine is decomposed $3N_2H_4=N_2+4NH_3$ above 350°. Hydrazine freezes at 0°, and its m.p. is 1·4°—there is much undercooling. F. Friedrichs gave 1·8° for the m.p. of hydrazine. T. Curtius and co-workers found that when the hydrate is strongly cooled, it furnishes crystalline plates which melt at —40°. The determination of the f.p. enables the mol. wt. of hydrazine in water to be calculated, and the result 68 is in agreement with the formula $N_2H_4.2H_2O$. C. A. Lobry de Bruyn found the b.p. of mixtures of hydrazine and water has a maximum at 120·5°, 771 mm. press., for a mixture with 58·5 per cent. of N_2H_4, and 41·5 per cent. of water.

M. Berthelot and C. Matignon found the heat of formation to be $(N_2,H_4,Aq.)=N_2H_{4soln.}-9{\cdot}5$ Cals.; hydrazine is an endothermal compound, and its conversion into ammonia liberates 51·5 Cals., and the reaction is not reversible. $N_2H_4.Aq.=NH_3.Aq.+N+H+25{\cdot}75$ Cals.; $3N_2H_4Aq.=4NH_3Aq.+N_2+98{\cdot}25$ Cals.; and $N_2H_4.Aq.+H_2=2NH_3Aq.+51{\cdot}5$ Cals. R. Bach gave for the formation of various combinations, $(N_2H_5OH,Aq.)=19{\cdot}19$ Cals.; $(N_2H_5.HSO_4,Aq.)=-85{\cdot}27$ Cals.; $(N_2H_5Cl,Aq.)=-54{\cdot}40$ Cals.; $(N_2H_5Cl.HCl,Aq.)=-62{\cdot}01$ Cals.; $(N_2H_5OHAq.,H_2SO_4Aq.)=113{\cdot}0$ Cals.; $(N_2H_5OHAq.,2HClAq.)=96{\cdot}0$ Cals.; $(N_2H_5OHAq.,HClAq.)=96{\cdot}5$ Cals.; $(N_2H_5OHAq.,2HNO_3Aq.)=97{\cdot}0$ Cals.; $(N_2H_5OHAq.,HNO_3Aq.)=97{\cdot}0$ Cals.; and for the heat of formation of hydrazine hydrate, $(N_23H_2,O)=561-644$ Cals. The fact that the heat of formation is a positive quantity shows that hydrazine hydrate is probably not the analogue of the diazo-compounds, but rather has the constitution $H_2N.NH_3.OH$, and not $H_3N.NH_2.OH$. The observed data just indicated shows that the hydrazine salts $N_2H_4.HR$ are not converted into $N_2H_4.2HR$ salts in aq. soln. since the heats of neutralization of hydrazine hydrate by either one or two eq. of the acid are the same. From this, it is probable that the salts $N_2H_4.2HR$ undergo hydrolytic dissociation in aq. soln., and this, taken in conjunction with the electrolytic dissociation which takes place at the same time, would explain the fact that the mol. wt. of these salts as determined by the cryoscopic method are only one-fourth of those expressed by their formulæ. J. Thomsen has discussed the thermochemistry of hydrazine. The heat of neutralization is less than that of ammonia, or hydroxylamine.

J. W. Brühl gave 8·867 for the mol. refraction, with the μ^2 formula (**1**, 11, 13) for Na-light, and for H_α-light, 8·82; and for the mol. dispersion, $M(\gamma-\alpha)=0·266$. According to R. Bach, the mol. refractions of hydrazine hydrate show that the at. refraction of nitrogen deduced from the mol. refraction of the hydrate is much smaller than the value obtained from the other hydrazine salts and other nitrogen compounds. The value for the two nitrogen atoms calculated for the formula $(n-1)/d$ is 9·5 in the case of the hydrate, and nearly 11 for the salts. In this behaviour, hydrazine resembles ammonia, as the latter aq. soln. also gives a very much smaller value for the at. refraction of nitrogen than that deduced from the ammonium salts or the amines.

E. C. Szarvasy found that on electrolysis of soln. of hydrazine hydrate, sulphate, or chloride, nitrogen and hydrogen were produced in quantities corresponding with the quantitative decomposition of the base; and J. W. Turrentine and coworkers found that with a high current density, and low temp., and strongly acid salt soln. of hydrazine sulphate furnished hydrazoic acid, and its formation was attributed to the persulphate-ions; in the case of hydrazine carbonate, under conditions which would favour the formation of percarbonates, the hydrazine suffered quantitative oxidation into nitrogen and water. In the electrochemical oxidation of hydrazine hydrochloride and hydrobromide, hydrazoic acid was not obtained under any conditions. At low temp. and with low current densities only nitrogen and water were produced, whilst at high temp. and with high current densities considerable quantities of ammonia were formed. In certain experiments with the hydrochloride, the conditions were such as should have led to the formation of chlorate ions. The production of chlorate seemed, however, to be rendered impossible owing to the reduction of the hypochlorite by the hydrazine present. S. Bodforss studied the electrolysis of soln. of hydrazine sulphate. E. Cohen and C. A. Lobry de Bruyn found for the smallest electrical conductivity of anhydrous hydrazine halides, 4×10^{-5} mho. The addition of ammonia increases the conductivity only slightly; and with water additions, the conductivity of hydrazine falls to a minimum with 60 molar proportions of water to 100 of hydrazine. G. Bredig gave for the mol. conductivity, μ, for a mol of the hydrate, $OH_4N.NH_3(OH)$, in v litres of water, at 25°:

v .	8	16	32	64	128	256	8	
μ .	1·33	1·56	1·93	2·53	3·57	5·14	224	
α .	0·594	0·70	0·86	1·13	1·59	2·30	—	per cent.
K_1 .	$0·0_544$	$0·0_530$	$0·0_523$	$0·0_521$	$0·0_520$	$0·0_521$	—	

The percentage degree of ionization, α; and the ionization constant K_1 are also indicated. Hence, the first ionization constant is rather weaker than that of ammonium hydroxide, being somewhere near $K_1=3\times10^{-6}$. I. M. Kolthoff calculated for the second ionization constant of hydrazine, $K_2=2·8\times10^{-3}$; and E. C. Gilbert said that it should be less than 10^{-12}. P. Drude gave 53 for the dielectric constant at 22°.

The chemical properties of hydrazine and its hydrates.—O. Löw found that hydrazine exerts an extremely poisonous action on organisms—seedlings, fungi, and infusoriæ. A subcutaneous injection of 0·1 mgrm. of hydrazine sulphate, neutralized with sodium carbonate, in a guinea-pig caused death in 2½ hrs.; and 0·5 grm. administered to a puppy, similarly, caused death in 2½ hrs. P. Borisoff reported that when subcutaneously injected in dogs, small doses (0·05 grm. of the hydrazine sulphate per kilo. of body weight) acted as a slight stimulant; and with large doses (0·1 grm. per kilo.) the stage of stimulation was more intense, and followed by depression, ending in coma and death in two days. Given by the mouth, it produced salivation and sickness. The heart went more quickly at first, then slowed gradually and became irregular. The respiratory movements reminded one of asthma. The temperature of the body sinks. The urine was strongly acid, and contained small quantities of the unchanged hydrazine, a small amount of albumin, in one case bile pigment, and in most cases considerable quantities of allantoin. The saliva, which is abundant, also contained allantoin. Observations on the subject were also made by F. P. Underhill and co-workers. M. Raciborsky showed that some fungi can assimilate hydrazine. Both hydrazine and its hydrate absorb moisture and carbon dioxide from **air.** Hydrazine is slowly attacked by **oxygen** with the liberation of nitrogen, and it burns with a blue flame in air; hydrazine hydrate slowly oxidizes in air with the liberation of nitrogen. F. D. Chattaway discussed the oxidation of aromatic hydrazines by air or free oxygen. E. J. Cuy and W. C. Bray said that the presence of oxygen is responsible for the fairly rapid decomposition of hydrazine in alkaline soln. Hydrazine and its hydrate are miscible with **water** in all proportions. K. Neundlinger studied the catalysis of hydrazine by platinum-black—*vide infra.* A. W. Browne and F. F. Shetterly found that **ozone** may react with hydrazine, forming hydrazoic acid, but no ammonia. W. Strecker and H. Theinemann observed that hydrazine hydrate is oxidized by ozone principally to nitrogen and water, only small quantities of ammonium and hydrazine nitrates being formed. A. W. Browne found that **hydrogen dioxide** in dil. sulphuric acid soln. forms a little hydrazoic acid when in the presence of a soln. of hydrazine: $3N_2H_4+5H_2O_2=2HN_3+10H_2O$. A. W. Browne and O. R. Overman found that the presence of ammonium sulphate does not increase, but rather decreases, the yield of hydrazoic acid when hydrazine sulphate is oxidized by hydrogen dioxide in sulphuric acid soln. C. Wurster found that phenylhydrazine is converted by hydrogen dioxide into benzene and diazobenzene imide. The production of benzene makes it probable that free diazobenzene is first formed in the oxidation of the hydrazine.

Hydrazine and its combinations are very powerful reducing agents. Some **oxidizing agents** oxidize aq. soln. of hydrazine to ammonia, NH_3, with the formation of but little hydrazoic acid, N_3H; and the other oxidizing agents give comparatively large yields of the acid and but little ammonia. According to C. A. Lobry de Bruyn, hydrazine inflames when in contact with **chlorine**; and with **bromine** and **iodine,** the corresponding haloid acids are produced, and nitrogen is set free. C. T. Dowell showed that nitrogen trichloride is probably formed when chlorine acts on hydrazine in contact with carbon tetrachloride. T. W. B. Welsh and H. J. Broderson found that iodine is very soluble in anhydrous hydrazine, and causes a rapid decomposition. With chlorine, a small amount of hydrazoic acid is formed in both acid and alkaline soln.; with bromine, mere traces in alkaline and none in acid soln.; and with iodine, no hydrazoic acid was observed. Alcoholic soln. of hydrazine hydrate and iodine react quantitatively: $5N_2H_4.H_2O+2I_2 \rightarrow 4N_2H_4.HI+N_2+5H_2O$, and hence the reaction could be utilized in finding the strength of soln. of hydrazine. Chlorine water and hydrazine sulphate react: $N_2H_4+2Cl_2=4HCl+N_2$, and hence, hydrazine sulphate can be utilized in the analysis of chloride of lime and Javelle water. The reaction with iodine was studied by E. Rupp, and R. Stollé from the point of view of volumetric analysis; and E. C. Gilbert studied the electrometric titration. Hydrazine hydrate reacts with **acids** to form salts—*vide infra,* hydrazine halides. E. Riegler studied the reduction of *iodic acid* by hydrazine sulphate; R. Stollé, E. Rupp, and H. Spiess showed that a soln. of iodine in the presence of sodium or potassium hydrocarbonate acts on hydrazine and its salts: $N_2H_4+2I_2=4HI+N_2$. F. W. O. de Coninck found that with **alkali hypochlorites,** there is a copious evolution of nitrogen. G. R. Levi represented the reaction with alkali **chlorites:** $N_2H_4.2HCl+NaClO_2=N_2+NaCl+2H_2O+2HCl$, though he prepared hydrazine chlorite by double decomposition. According to A. W. Browne and F. F. Shetterly, and W. R. Hodgkinson, **chlorates, bromates,** and **iodates** are not reduced by hydrazine, unless in the presence of small amounts of silver sulphate, metallic copper, copper oxide, or a copper salt. K. A. Hofmann observed that a neutral or slightly acid soln. of potassium chlorate in the presence of a trace of osmium tetroxide readily decomposes hydrazine sulphate to nitrogen, etc. A. W. Browne and F. F. Shetterly, and W. R. Hodgkinson noticed that other metals which change easily from an -ic to -ous condition also act catalytically: $2KClO_3+3N_2H_4 \rightarrow 6H_2O+3N_2+2KCl$. The reaction is rapid in acid soln., but very slow in neutral or alkaline soln. The reaction has been recommended for estimating the total chlorine, bromine, or iodine in the respcctive chlorates, bromates, or iodates—the excess of hydrazine can be destroyed by permanganate soln. acidified with nitric acid. The reaction between hydrazine sulphate and potassium iodate, $5N_2H_4.H_2SO_4+4KIO_3 \rightarrow 5N_2+12H_2O+2K_2SO_4+3H_2SO_4+2I_2$, has been recommended by E. Rimini for the determination of hydrazine; but the reaction with the chlorates and bromates is not quantitative. T. Curtius and H. Schulz, M. Schlötter, P. Jannasch and A. Jahn, F. Fischer and W. F. Tschudin, and A. Kurtenacker and J. Wagner, studied the oxidation of hydrazine by bromates; and E. C. Gilbert, the electrometric titration of hydrazine with potassium bromate. A. W. Browne and F. F. Shetterly found that hydrazine is in part converted to hydrazoic acid by **potassium perchlorate,** and by **sodium periodate.** W. R. Hodgkinson said that perchlorates are not reduced in the same way as the chlorates; hydrazine nitrate and **ammonium perchlorate** may be fused together without reacting.

T. Curtius and co-workers, and T. W. B. Welsh and H. J. Broderson found that hydrazine or its hydrate slowly dissolves **sulphur** with the development of much heat, and the formation of a brown liquid which smells like ammonium sulphide and deposits sulphur when treated with water. A 23 per cent. aq. soln. of hydrazine, when boiled with sulphur, gives off hydrogen sulphide. F. Ephraim and H. Piotrowsky found that the reaction in a short time is $N_2H_4+2S=N_2+2H_2S$. H. Piotrowsky represented the reaction $N_2H_4+2S=N_2+2H_2S$, and a side reaction, $2N_2H_4+S=N_2+2NH_3+H_2S$, **hydrogen sulphide** readily dissolves in hydrazine hydrate, but no solid is produced; with anhydrous hydrazine, H. Piotrowsky believes that hydrazine hydrosulphide, $2N_2H_4.H_2S$, is formed with a dissociation press. of 760 mm. at 35°. H. Piotrowsky represented the reaction with **thionyl chloride,** $SOCl_2+4N_2H_4=SO(NH.NH_2)_2+2N_2H_5Cl$; the reaction with **sulphur dioxide** results in the formation of **hydrazine disulphinic acid,** $SO_2H.NH.NH.SO_2H$, which forms salts, $(HN.SO_2)_2Ba$ and $Ba(N.SO_2)_2Ba$; and with **sulphur trioxide,** there is formed sulphur dioxide, sulphur, and sulphur sesquioxide, S_2O_3. With **sulphur dioxide,** hydrazine forms the hydrazine salt of an unknown acid, **hydrazine disulphuric acid,** $SO_2H.NH.NH.HSO_2$, by direct addition: $2SO_2+3N_2H_4=N_2H_2(HSO_2.N_2H_4)_2$; **thionyl chloride** is reduced to sulphur, which dissolves in the excess of hydrazine, forming **sulphohydrazinium.** H. T. Bucherer and co-workers studied the action of **sulphites** on the hydrazines. Anhydrous hydrazine absorbs **sulphur trioxide** when exposed to the vapour of this compound diluted with much air, and **hydrazine sulphonic acid,** $N_2H_3.HSO_3$, is formed. Barium and calcium salts have been prepared directly from the acid, while the alkali, silver, and ammonium salts are obtained by double decomposition with the former. If hydrazine sulphonic acid be powdered and mixed in small portions at a time with a well-cooled soln. of potassium nitrate, flat prisms of the potassium salt of **azidosulphonic acid,** N_3SO_3H, are formed. The crystals explode when heated, and the aq. soln. is decomposed into hydrazoic acid, N_3H, and sulphuric acid when treated with mineral acids. Hydrazine reduces **sulphuric acid** to hydrogen sulphide—*vide infra,* hydrazine sulphates. A. W. Browne and F. F. Shetterly found that hydrazine is partly oxidized to hydrazoic acid by **persulphates,** and partly to nitrogen, according to E. Pannain: $2K_2S_2O_8+N_2H_4.H_2SO_4+6KOH=5K_2SO_4+N_2+6H_2O$. E. Rimini gave: $N_2H_4.KHSO_4+5KOH+2K_2S_2O_8=N_2+5K_2SO_4+5H_2O$. W. R. Hodgkinson made some observations on this subject. A. W. Browne and F. F. Shetterly found that hydrazine gives no hydrazoic acid with **selenious acid,** but **selenic acid** gives an appreciable quantity; and **telluric acid** gives much hydrazoic acid and ammonia.

According to A. W. Browne and co-workers (T. W. B. Welsh, and A. W. Browne and A. E. Houlehan), the amminolysis of hydrazine sulphate or selenate occurs when the salt is treated with liquid **ammonia:** $N_2H_4.H_2SO_4+2NH_3=(NH_4)_2SO_4+N_2H_4$. F. Friedrichs found the reaction is quantitative, and he was not able to detect any sign of chemical combination between ammonia and hydrazine. His measurements of the temp., θ; vap. press., p mm. of the sat. soln.; and of the conc., C, of the sat. soln. with solid hydrazine in equilibrium with the ammonia; and the conc., C_1, of the sat. soln. with solid ammonia in equilibrium are shown in Table XXIX,

TABLE XXIX.—PRESSURE, TEMPERATURE, AND CONCENTRATION RELATIONS OF THE BINARY SYSTEM: NH_3–N_2H_4

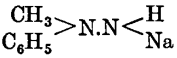
θ	p	C	C_1	θ	p	C
−80°	40	13·0	13·0	−30°	562	63·8
−79°	42	13·5	8·5	−25°	630	69·8
−78°	45	14·0	0·0	−20°	675	76·0
−75°	55	15·5	—	−19°	680	77·0
−70°	78	19·5	—	−18°	682	77·9
−65°	106	23·9	—	−17°	682	79·3
−60°	145	29·1	—	−16°	680	80·2
−55°	197	33·8	—	−15°	677	81·6
−50°	252	39·7	—	−10°	620	87·6
−45°	320	45·0	—	− 5°	470	92·6
−40°	395	51·0	—	− 0°	175	98·0
−35°	480	57·1	—	− 1°	105	98·6

where the conc. are expressed in percentages of ammonia. Hydrazine dissolves ammonia gas. R. Stollé found that **sodamide** with an excess of hydrazine hydrate reacts: $N_2H_4.H_2O+NH_2Na=N_2H_4+NH_3+NaOH$; and if the sodamide be in excess, **sodium hydrazine** is formed: $N_2H_4+NaNH_2=NH_3+NaN_2H_3$. According to K. A. Hofmann and R. Kroll, hydrazine hydrochloride decomposes at 200° into ammonium and hydrogen chlorides and nitrogen in the presence of **hydroxylamine hydrochloride,** a reaction occurs at about 150° and, with suitable proportions of the reactants, follows the course: $2NH_2.OH+N_2H_4.2HCl=2NH_4Cl+N_2+2H_2O$. The absence of nitrous oxide from the products indicates the quantitative participation of hydroxylamine in the change and the probable preliminary formation of a very unstable salt of diaminohydrazine. E. Ebler and R. L. Krause obtained a product which explodes at 70°, by the action of ethereal soln. of hydrazine on **zinc diamide,** or by the action of **zinc ethyl** and hydrazine. The composition is ZnN_2H_2, or **zinc hydrazine.** T. Curtius observed that hydrazine hydrate reacts vigorously with **nitrous acid** and the *nitrites*, forming, under some conditions, hydrazoic acid (*q.v.*), under others hydrazine nitrite (*q.v.*). The reaction was studied by J. de Girard and A. de Saporta, B. B. Dey and H. K. Sen, and F. Sommer. C. A. Lobry de Bruyn found that **nitrous oxide** reacts with hydrazine. J. de Girard and A. de Saporta symbolized the reaction $N_2H_4.H_2SO_4+2NaNO_3=N_2+Na_2SO_4+2HNO_2+2H_2O$; but E. Francke prefers, $N_2H_4+HNO_2=N_2O+NH_3+H_2O$. The mechanism of the reaction was studied by F. Sommer and H. Pincas, A. W. Browne and O. R. Overman, F. Sommer, A. Angeli, E. Oliveri-Mandala, E. Francke, T. Curtius, M. Dennstedt and W. Göhlich, etc. The action of nitrites was studied by B. B. Dey and H. K. Sen; and the action of nitrous esters, by M. Betti, R. Stollé and J. Thiele. Larger yields of hydrazoic acid and smaller yields of ammonia were obtained by A. W. Browne and O. R. Overman during the oxidation of hydrazine sulphate by potassium nitrate than in the case with hydrogen dioxide. For the action of **nitric acid,** *vide* hydrazine nitrate. White **phosphorus** reacts with hydrazine or its hydrate, and the soln. becomes yellow, reddish-violet, and black; the smell of phosphine is then perceptible. When the black liquid is diluted with water, a black precipitate is formed, which C. A. Lobry de Bruyn considered to be a solid phosphorus hydride. The reaction was studied by J. W. Dito. For the action of **phosphoric acid,** see hydrazine phosphates. A. W. Browne and F. F. Shetterly found that **arsenious oxide** with hydrazine gives hydrazoic acid and ammonia. W. R. Hodgkinson studied the action of **arsenates** on hydrazine. C. A. Lobry de Bruyn found that hydrazine and its hydrate react with **carbon dioxide**; and there is a vigorous reaction with **carbonyl chloride.** Hydrazine and its hydrate are soluble in **methyl, ethyl, propyl, butyl, and amyl alcohols,** but they are not soluble, or only slightly soluble in the usual organic solvents. W. Schlenk and T. Weichselfelder found that hydrazine reacts with methyl alcohol, and the soln., on cooling, furnishes colourless leaflets of **hydrazine methyl alcoholate,** $(NH_2.NH_3)OCH_3$, isomeric with methylhydrazine hydrate, $(NH_2.NH_2CH_3)OH$. A. Angeli found that the action of **cyanogen** on hydrazine produces a substance with the composition $C_2N_6H_8$. G. Pellizzari and co-workers found that with **cyanogen chloride or bromide,** hydrazine in aq. soln. furnishes diaminoguanidine, $NH : C(NH.NH_2)_2$. E. J. Cuy and W. C. Bray found that in alkaline soln., hydrazine is quantitatively oxidized to nitrogen by **potassium ferrocyanide,** R. von Rothenburg found that **chloroform** is not acted on in boiling soln., while **iodoform** is slightly attacked.

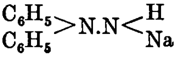
J. Houben obtained methane, etc., by the action of *magnesium alkyl haloids* on the hydrazines; the action of *zinc ethyl* and magnesium alkyl haloids on hydrazine has been studied by R. L. Krause; the action of mono- and di- *chloroacetic acids,* by M. Busch and E. Meussdörffer; *ethyl chloroacetate,* by A. Reissert and W. Kayser, and M. Busch and co-workers; *phenylglyoxalic acid,* by A. Elbers; *dinitrophenylhydrazine,* by T. Curtius and M. Mayer; *ethyl dinitrobenzoate,* by T. Curtius and A. Riedel; *dinitrobenzoic acid,* by T. Curtius and H. F. Bollenbach; *nitro- and amido-phthalhydrazides,* by T. Curtius and A. Hoesch; *formaldehyde,* by E. Riegler, and E. Rimini; *carbonyl* compounds, by H. Standinger and O. Kupfer; *dicyanodiamide,* by K. A. Hofmann and O. Ehrard; *fats,* by P. Falciola and A. Mannino; *nitriles,* by E. Müller and L. Herrdegen, W. F. Donath, I. Lifschitz, and T. Curtius and co-workers; *chloral hydrate* and *bromal hydrate,* by G. Knöpfer; *nitroso-bases,* by O. Fischer and co-workers, and R. von Rothenburg; *chloroketones,* by S. Bodforss; *imido-ethers,* by A. Pinner; *thiamides,* by A. Junghahn and co-workers; *ethylene bromide,* by R. Stollé; *thiocarbamides,* by M. Busch and co-workers; *oxalacetic acid,* by H. J. H. Fenton and H. O. Jones; *acetonyl acetone,* by T. Gray; *methyl butyrylacetoacetates,* by A. Bongert; *methylethylacraldehyde,* by F. Demmer; *lactones,* by J. Wedel; *acetic anhydrides,* by R. Stollé; *chloro- and bromo-anilic acids,* by A. Descomps; *phenols,* by L. Hoffmann; *acetamide,* by M. O. Forster; *nitrodiazobenzene,* by H. von Pechmann; *picrylic chloride,* by A. Purgotti; *benzoic chloride, methyl iodide, ethyl iodide,* and *isoamyl chloride,* by R. von Rothenburg; *metaphosphoric and phosphorous esters,* by W. Strecker and H. Heuser; etc.

Hydrazine attacks *indiarubber,* and *cork;* and, when boiled in aq. soln., *glass* is eroded. Hydrazine hydrate and **sodium** develop much heat, with the expulsion of hydrogen and ammonia. When the liquid cools, a crystalline substance is formed which is soluble in water and alcohol, and which is thought to be *sodium hydrazide hydroxide,* N_2H_5ONa. The aq. soln. gives the reactions for hydrazine. T. Weichselfelder prepared the derivatives:

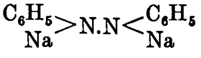
$\begin{matrix}CH_3\\Na\end{matrix}>N.N<\begin{matrix}H\\H\end{matrix}$



$\begin{matrix}CH_3\\C_6H_5\end{matrix}>N.N<\begin{matrix}H\\Na\end{matrix}$

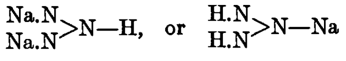


$\begin{matrix}C_6H_5\\C_6H_5\end{matrix}>N.N<\begin{matrix}H\\Na\end{matrix}$



$\begin{matrix}C_6H_5\\Na\end{matrix}>N.N<\begin{matrix}C_6H_5\\Na\end{matrix}$

According to E. Scandola, when hydrazine is added drop by drop to finely granulated sodium suspended in ether, and then heated on a water-bath with a reflux condenser, a white substance is formed which explodes in air. If left in contact with the ether, it loses its explosive property. The white compound does not act on silver nitrate in ammoniacal soln. Its structure is supposed to correspond with *sodium triimide* or **sodium hydrazide :**



$\begin{matrix}Na.N\\Na.N\end{matrix}>N—H, \text{ or } \begin{matrix}H.N\\H.N\end{matrix}>N—Na$

This substance was studied by T. W. B. Welsh, who found that the electrolysis of soln. of sodium hydrazide in anhydrous hydrazine furnishes nitrogen and hydrogen at both the anode and cathode. For each atom of copper deposited on the coulometer cathode, 1·1–1·5 atoms of nitrogen were liberated at the anode when the soln. were fairly dil., but in the case of more conc. soln. the ratio Cu : N was lower, and had an average value of 1 : 2·4. Sodium hydrazine, $NH_2.NHNa$, was obtained in glistening leaflets by W. Schlenk and T. Weichselfelder. "A mere breath of air or a trace of moisture or alcohol sufficed to produce a disastrous explosion." E. Ebler and E. Schott found that **zinc** partly immersed in hydrazine hydrate while exposed to air, furnishes white crystalline *zinc hydrazinecarboxylate dihydrazinate*, $(NH_2.NH.CO.O)_2{=}Zn{=}(NH_2.NH_2)_2$, and hydrogen is evolved. In the presence of **platinum**, aq. soln. of hydrazine are catalytically decomposed: $2N_2H_4 = 2NH_3 + N_2 + H_2$. S. M. Tanatar found that if sodium hydroxide be present, the reaction is to be symbolized: $3N_2H_4 = 2NH_3 + 2N_2 + 3H_2$; and if sulphates be present, $3N_2H_4 = 4NH_3 + N_2$. A. Gutbier and K. Neundlinger found no evidence of the formation of hydrogen or of nitrous oxide; hydrogen is formed in the presence of barium hydroxide and alkali hydroxides. They thus explain the reaction: the hydrazine breaks up into hydrogen and nitrogen in the presence of platinum black; the nascent hydrogen then reduces two mols. of hydrazine to ammonia. Should, however, the dissociation of the hydrazine hydrate be prevented by the presence of a strong base, the reducing action of the nascent hydrogen is retarded, and consequently free hydrogen is liberated. The velocity of the decomposition of hydrazine is proportional to the quantity of the catalyst present, and is uninfluenced by glass. The hydrazine can only be decomposed to the extent of 93 per cent. The order of reaction could not be determined, but is shown to depend on the condition of the platinum-black. A. Purgotti and L. Zanichelli showed that a soln. of hydrazine sulphate is not decomposed catalytically if the platinum-black has been boiled in water for four hours. This fact makes it appear as if it is the occluded oxygen which induces the catalytic process, and this inference is confirmed by the restoration of the activity of the platinum black if it be dried in air. Immersion in hydrogen dioxide does not restore its activity. Platinum black which is inactive towards hydrazine may still stimulate the decomposition of hydrogen dioxide and hydroxylamine, showing that the mechanism of the reaction is probably different. A. Purgotti and L. Zanichelli found that the velocity of decomposition increases nearly proportionately to the increase in the amount of platinum present, and roughly also to the increase of conc. The rate of decomposition by platinum of aq. salts of hydrazine varies greatly with the nature of the acid; the monohydrochloride, sulphate, nitrate, and hydrobromide are most rapidly affected and in the order given, whilst the diacetate, dihydrochloride, and dihydrobromide are much less readily decomposed. The addition of traces of acids has a very varying influence on the catalysis; sulphuric, hydrochloric, phosphoric, and boric acids have little effect, but hydrofluoric, hydrobromic, hydriodic, and nearly all organic acids very much retard, if they do not completely inhibit, decomposition. These facts explain the varying nature of the catalysis of hydrazine salts in soln. A. P. Sabanéeff found that if oxygen be passed into a soln. of hydrazine sulphate in which platinum-black is suspended, the following reaction occurs in the course of one or two hours: $4N_2H_4.H_2SO_4 + 5O = 3N_2 + 5H_2O + 3H_2SO_4 + (NH_4)_2SO_4$. K. Neundlinger studied this subject.

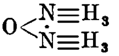
Anhydrous hydrazine dissolves many **salts**, thus, 100 parts of solvent at 12·5°–13° dissolve 12·2 parts of *sodium chloride;* 8·5, of *potassium chloride;* 56·4, of *potassium bromide;* 135·7, of *potassium iodide;* 26·6, of *sodium nitrate;* 21·7, of *potassium nitrate;* and 81·1, of *barium nitrate.* The hydrazine seemed to unite with sodium chloride; with a warm soln. of *ammonium chloride,* ammonia is evolved, and in the cold, there seems to be a state of equilibrium; a complex salt seems to be formed with *lead nitrate.* An aq. soln. of hydrazine hydrate also dissolves a number of salts, potassium bromide and iodide, *ammonium sulphate, potassium cyanide,* barium nitrate, *magnesium sulphate,* etc. According to T. W. B. Welsh and H. J. Broderson, the solubility of the metal haloids seems to increase with the increase of at. wt. of the halogen; in the case of the haloids of the alkali earth metals, crystalline substances separate from the soln., which are probably hydrazinated salts. The carbonates are either insoluble or very slightly soluble. The oxides are all insoluble. The nitrates are mostly soluble, with the exception of those which react with the solvent. Sulphides and sulphates are but slightly soluble. Ammonium salts, except triammonium phosphate, dissolve with evolution of ammonia. Bismuth chloride dissolves, and reacts with the hydrazine, bismuth being quantitatively precipitated. Cadmium carbonate and sulphide are insoluble, but the haloids are very soluble. Mercury sulphide is insoluble, but the other mercury salts react immediately with the solvent, and mercury is precipitated. Nickel and cobalt salts dissolve, and react with the solvent to form hydrazine additive compounds. In the case of cobalt chloride, a cobalt mirror is gradually formed. Copper and lead salts dissolve with more or less decomposition. Silver salts invariably yield a silver mirror.

A great many salts are reduced by hydrazine and its salts; thus, T. Curtius found that neutral copper sulphate, and Fehling's soln. give a dense, red precipitate. According to A. W. Browne and F. F. Shetterly, the azure-blue soln. of a copper salt containing an excess of ammonia, is rapidly decolorized by warming it with hydroxylamine or hydrazine salts owing to the reduction of ammino-cupric sulphate, $Cu(NH_3)_4SO_4$, to ammino-cuprous sulphate, $Cu_2(NH_3)_4SO_4$, with the evolution of nitrogen gas: $4Cu(NH_3)_4SO_4+N_2H_4H_2SO_4 \rightarrow 2Cu_2(NH_3)_4SO_4 +3(NH_4)_2SO_4+2NH_3+N_2$. The colourless soln., in the absence of an excess of reducing agent, is gradually coloured blue by exposure to air or by treatment with an oxidizing agent—*e.g.* hydrogen peroxide. If the colourless soln. be acidified and treated with potassium iodide or potassium thiocyanate, colourless cuprous iodide or thiocyanate is respectively precipitated directly. A. Purgotti represented the reaction in a boiling soln. of hydrazine and copper sulphates, and sodium chloride, $4CuSO_4+10NaCl+N_2H_4.H_2SO_4=4CuCl+5Na_2SO_4+6HCl+N_2$. T. Curtius found that when hydrazine is added to a soln. of ammoniacal **silver nitrate,** a precipitate of metallic silver is formed; and with an acid soln. of **gold chloride,** the metal is deposited. The reaction was studied by F. Schrader. The dehydrating action of **sodium hydroxide,** and of **barium oxide or hydroxide,** has been discussed in connection with the preparation of anhydrous hydrazine. A. Stähler suggested that **calcium oxide or hydroxide** forms either a solid soln. or a **calcium oxyhydrazide,** $Ca(ON_2H_5)_2$, which easily decomposes into calcium oxide and hydrazine. F. Schrader studied the action of **magnesium oxide.** When hydrazine hydrate is dropped on **mercuric oxide,** an explosion may occur. A. W. Browne and F. F. Shetterly said that an acid or alkaline soln. of hydrazine sulphate heated with red mercuric oxide gives neither ammonia nor hydrazoic acid, but when the yellow oxide is used with a slightly alkaline solu. at 0°, appreciable quantities of both ammonia and hydrazoic acid are formed. C. F. Hale and V. E. Nunez gave for alcoholic soln. of hydrazine, $N_2H_4.H_2O+2HgO =N_2+2Hg+3H_2O$. A soln. of **mercuric chloride** oxidizes hydrazine, forming neither ammonia nor hydrazoic acid. Solutions of mercuric salts, in the presence of mineral acids, are not reduced by hydroxylamine or hydrazine salts, but in a soln. of acetic acid in the presence of sodium acetate, heating with a hydrazine salt leads to the gradual precipitation of all the mercury: $2HgCl_2+N_2H_4 \rightarrow 4HCl +N_2+2Hg$. Ammoniacal soln. of mercuric salts are reduced immediately. E. Rimini gave for alkaline soln.: $N_2H_4.NaHSO_4+2HgCl_2+5NaOH=4NaCl +Na_2SO_4+2Hg+N_2+5H_2O$. The addition of a soln. of hydrazine chloride in a mixture of alcohol and ether to a similar soln. of mercuric chloride gives a white flocculent precipitate of $N_2H_4.HgCl_2$, which by contact with water forms $N_2H_2.Hg_2Cl_2$. An aq. soln. of hydrazine nitrate with mercuric nitrate furnishes $N_2H_4.Hg(NO_3)_2$, and with mercurous nitrate, $N_2H_4.Hg_2(NO_3)_2$. All these mercury compounds are explosive. O. Diels and S. Uthemann studied the action of mercuric oxide on various hydrazines; and N. R. Dhar, the induced reaction involving the effect of hydrazine on the reduction of mercuric chloride by oxalic acid. A. Benrath and K. Ruland observed that ceric sulphate in the presence of sulphuric acid oxidizes hydrazine in accord with the equation: $2N_2H_4+2Ce(SO_4)_2=N_2+(NH_4)_2SO_4+Ce_2(SO_4)_3$. A. W. Browne and F. F. Shetterly found **ammonium metavanadate** oxidizes hydrazine partly to hydrazoic acid, and partly so that the remaining nitrogen is evolved as nitrogen. K. A. Hofmann and F. Küspert used **vanadic sulphate** for a volumetric analytical process, the vanadyl sulphate produced being determined by titration of the soln. with potassium permanganate. T. Curtius and co-workers noted that hydrazine hydrate reduces **manganates** or **permanganates** to manganese dioxyhydrate; and I. M. Kolthoff said that in alkaline soln. or in a boiling hydrochloric acid soln., an excess of permanganate reduces hydrazine to nitrogen and ammonia. J. Petersen represented the reaction in the presence of 6–12 per cent. sulphuric acid by $17N_2H_4+13O=13H_2O+14NH_3+10N_2$; U. Roberto and F. Roncali, by $2KMnO_4+3H_2SO_4=K_2SO_4+2MnSO_4+5O+3H_2O$, and $5(N_2H_4.H_2SO_4)+5O_2=10H_2O+5H_2SO_4+5N_2$; but L. Medri prefers J. Petersen's equation. A. Purgotti represented the reaction with **manganese dioxide** in acid soln. by $2MnO_2+H_2SO_4+N_2H_4.H_2SO_4=2MnSO_4+4H_2O+N_2$; in neutral soln., a similar reaction occurs but hydrazine hydrate is formed. A. W. Browne and F. F. Shetterly observed that little ammonia and hydrazoic acid are formed in the oxidation of hydrazine by magnesium dioxide. A. W. Browne and F. F. Shetterly, and J. Petersen noted that a small proportion of hydrazoic acid is produced under certain conditions. The reaction was studied by F. Schrader. E. J. Cuy and M. E. Rosenberg believed that the presence of manganous salt formed during the reaction between hydrazine and potassium permanganate in acidic soln. is responsible for the fact that the amount of oxidizing agent needed for 1 mol. of hydrazine is variable, and is always much lower than the four eq. required for oxidation to nitrogen. The mechanism of the reaction depends on the intermediate formation of manganic salt, and the ionic equation $N_2H^{\cdot}_5+Mn^{\cdot\cdot\cdot}=NH^{\cdot}_4+\frac{1}{2}N_2+H^{\cdot}+Mn^{\cdot\cdot}$. According to F. Raschig, when hydrogen in hot sulphuric acid soln. is oxidized by **potassium permanganate,** ammonium sulphate is formed. A. W. Browne and F. F. Shetterly obtained a little hydrazoic acid by the action of **chromic sulphate,** and of **potassium chromate** on hydrazine. T. Curtius and co-workers, and F. Schrader found that solid **chromic anhydride** explodes in contact with a drop of hydrazine hydrate, and that **chromates** are reduced by aq. soln. of hydrazine, forming chromic hydroxide. A. Purgotti represented the reaction: $2K_2Cr_2O_7+5H_2SO_4+3(N_2H_4.H_2SO_4)=2Cr_2(SO_4)_3+2K_2SO_4+14H_2O+3N_2$ in soln. of sulphuric acid. L. Medri, and W. R. Hodgkinson also studied this reaction. E. J. Cuy and W. C. Bray found that the oxidation of hydrazine to nitrogen is only quantitative with an excess of potassium dichromate and a moderate amount of acid. T. Curtius and F. Schrader found that the **molybdates** are reduced by a soln. of hydrazine hydrate. A. W. Browne and F. F. Shetterly showed that in acid soln. **molybdenum trioxide** yields appreciable quantities of both hydrazoic acid and ammonia. The action of hydrazine salts on **tungstates** was studied by F. Schrader; and the action on tungstates, molybdates, and **tantalates** was studied by W. R. Hodgkinson.

According to T. Curtius, **ferric chloride** is reduced by hydrazine to ferrous chloride; a reaction investigated by E. Müller and G. Wegelin, and F. Schrader. E. J. Cuy found that in the reaction between hydrazine and a ferric salt in acid soln., one mol of hydrazine requires between one and two eq. of ferric salt for oxidation. The limiting reaction may be expressed as follows: $N_2H^{\cdot}_5+Fe^{\cdot\cdot\cdot}=NH^{\cdot}_4+\frac{1}{2}N_2+H^{\cdot}+Fe^{\cdot\cdot}$. A. W. Browne and F. F. Shetterly showed that **ferric oxide** and hydrazine in aq. soln. yield ammonia, but no hydrazoic acid, while **nickel sesquioxide** and **cobalt sesquioxide** yield ammonia and traces of hydrazoic acid. H. Franzen and O. von Mayer made complex cobalt salts—*e.g.* $CoCl_2(N_2H_4)_2$, etc.—with hydrazine in place of ammonia. T. Curtius found that platinum is precipitated when a soln. of hydrazine is added to a neutral soln. of **platinum**

chloride. W. R. Hodgkinson studied the action of hydrazine on **osmates.** L. A. Tschugaeff and M. Grigorieff found that hydrazine hydrate readily reacts with **platinum diamminodichloride,** forming a series of hydrazine derivatives.

The constitution of hydrazine.—As indicated above, the analyses and vapour density of hydrazine hydrate agree with $N_2H_4.H_2O$; the lowering of the f.p. of water agrees with the presence of $N_2H_4.2H_2O$ in aq. soln.; and, as J. W. Brühl, and R. Bach have shown, the mol. refraction of hydrazine is in agreement with the assumption that the nitrogen atoms are tervalent. Hydrazine itself is therefore supposed to be constituted $H_2{=}H{-}N{=}H_2$, and the monohydrate, as $H_2{=}N{-}NH_3{-}OH$, with one ter- and one quinquivalent nitrogen atom, or with two quinquivalent nitrogen atoms.



$$O<\begin{matrix}N\equiv H_3\\ \dot{N}\equiv H_3\end{matrix}$$

The chief uses of hydrazine depend on its strong reducing powers; on its introducing no fixed constitution into the soln.; and on its faculty of condensing with many compounds—*e.g.* the aldehydes—to form sparingly soluble compounds which easily crystallize. E. E. Jelley recommended their use as photographic sensitizing agents. The use of hydrazine in analytical work has been discussed by E. Knoevenagel and E. Ebler, P. Jannasch and co-workers, M. Schlötter, U. Roberto and F. Roncali, A. Purgotti, J. de Girard and A. de Saporta, by J. Schmidt in his *Die Anwendung der Hydrazine in der analytischen Chemie* (Stuttgart, 1907); by E. Elber in his *Ueber die Anwendbarkeit der Hydroxylamin- und Hydrazinsalze in der qualitativen Analyse,* Heidelberg, 1902; and his *Analytische Operation mit Hydroxylamin- und Hydrazinsalze* (Heidelberg, 1905); and by K. Biedermann, *Ueber quantitative Metalltrennungen mit Hydrazin* (Heidelberg, 1900).

Some analytical reactions of hydrazine.—When an aq. soln. of hydrazine is shaken with benzaldehyde, $C_6H_5.CO.H$, in acid or alkaline soln., a flocculent, sparingly-soluble precipitate of *benzalazine,* $C_6H_5.CH:N.N:CH.C_6H_5$, is formed. Copper sulphate soln. gives a sparingly soluble blue precipitate of $CuSO_4.N_2H_4.H_2SO_4$. According to L. M. Dennis and A. W. Browne, hydrazine is best detected by oxidizing it to hydrazoic acid, and identifying the latter by the ferric chloride test of T. Curtius and co-workers where a soln. of iron-alum or ferric chloride gives a sharp red coloration with sodium azide—unlike the red formed with thiocyanates, this colour is discharged with hydrochloric acid. The oxidation is effected by treatment with ethyl nitrite in the presence of an alkali. To detect hydroxylamine, hydrazine and ammonia in the presence of one another, T. Curtius and F. Schrader treated the acidified soln. with gold chloride, when, if but $\frac{1}{40000}$th of hydrazine be present, gold will be reduced; if the filtrate from the gold is made alkaline, a further reduction of the gold indicated the presence of hydroxylamine. If ammonia be also present, V. Meyer recommended treating the original soln. with benzaldehyde, removing the benzalazine by an ether extraction, and separating the hydroxylamine and ammonia by treatment with platinum chloride. To determine the amount of hydrazine in an acid soln., J. Petersen titrated it with permanganate; E. Rimini titrated the iodine liberated from potassium iodate—*vide supra*—with thiosulphate; and R. Stollé titrated hydrazine salts in the presence of an excess of sodium bicarbonate, with a standard of iodine—ammonium salts were supposed to be absent. E. Petersen measures the volume of nitrogen given off when the hydrazine soln. is treated with an ammoniacal soln. of a copper salt; K. A. Hofmann and F. Küspert used a sulphuric acid soln. of vanadic acid in the same way: $N_2H_4+O_2 \rightarrow N_2+2H_2O$; and E. Rimini warmed an alkaline soln. of hydrazine and mercuric chloride: $N_2H_4.H_2SO_4+6KOH+2HgCl_2 \rightarrow K_2SO_4+4KCl+6H_2O+2Hg+N_2$, and likewise measured the gas evolved.

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§ 27. The Salts of Hydrazine, or Hydrazonium Salts

Hydrazine is strongly basic, and it forms two series of salts so that it can be regarded as a diacidic base. In general, however, with salts prepared in the ordinary way hydrazine behaves like a monoacidic base. In salts of the monoacidic series the hydrazinium radicle, so to speak, is the monad group, N_2H_5' ; and in the other series, the dyad group N_2H_6''. These groups are supposed to be respectively constituted :

$$\begin{array}{lcl} H_2{=}N & \qquad\qquad & H_3{\equiv}N- \\ H_3{\equiv}\dot{N}- & & H_3{\equiv}\dot{N}- \end{array}$$

G. Bredig,[1] and R. Bach concluded that while the first acidic function is nearly the same as that of ammonium hydroxide, the second acidic function of the base is so weak in aq. soln. that the corresponding salts are almost completely hydrolyzed. T. Curtius and H. Schulz said that a dihydrate exists in aq. soln. because the cryoscopic data gave a mol. wt. of 68. These data, however, can be interpreted on the basis either of a monohydrate or of a dihydrate. All this does not decide whether hydrazine is a monoacidic or a diacidic base. E. C. Gilbert also found that in the electrometric titration of a 0·1*M*-soln. of hydrazine hydrate with acids, there is only one point of inflection, Fig. 51. The *x* indicates where the second inflection would occur. Each division on the ordinate represents 100 millivolts.

T. Curtius and H. Schulz prepared **hydrazine difluoride,** $N_2H_6F_2$, by adding hydrofluoric acid to an alcoholic soln. of hydrazine hydrate; and also by evaporating an aq. soln. of the base neutralized with hydrofluoric acid. *Hydrazine monofluoride,* N_2H_5F, has not been prepared. The difluoride furnishes cubic crystals which melt at 105°, and sublime undecomposed. The salt is readily soluble in water; sparingly soluble in alcohol; and insoluble in ether, and benzene.

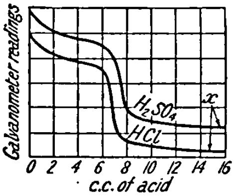


FIG. 51.—Electrometric Titration of Solutions of Hydrazine with Acids.

T. Curtius and H. Schulz prepared **hydrazine monochloride,** N_2H_5Cl, by heating the dichloride to 140°–160°; R. von Rothenburg obtained it by the action of hydrazine hydrate on benzoyl chloride; and F. Raschig, by the action of ammonia on monochloroamine, and by the action of hypochlorites on aq. ammonia. The long, needle-like crystals melt at 89°. The heat of neutralization, heat of soln., and heat of formation were measured by M. Berthelot and C. Matignon, and R. Bach as indicated in connection with hydrazine; R. Bach also measured the mol. refraction—*vide* hydrazine. T. Curtius and co-workers found that the salt is readily soluble in water, sparingly soluble in boiling alcohol, and the soln. on cooling furnishes well-developed crystals. According to F. Friedrichs, the monochloride is readily soluble in liquid ammonia and the soln. separates into two layers. Double salts with zinc, cadmium, mercury, tin, copper, and platinum were described by T. Curtius and F. Schrader, and F. Ranfaldi.

By treating an alcoholic soln. of hydrazine hydrate with chlorine, T. Curtius and H. Schulz prepared **hydrazine dichloride,** $N_2H_6Cl_2$, part of the hydrazine is at the same time decomposed: $3(N_2H_4.H_2O)+2Cl_2=3H_2O+N_2+2N_2H_6Cl_2$. T. Curtius obtained it by double decomposition of the sulphate with barium chloride; R. von Rothenburg, by the action of hydrazine hydrate on benzoyl chloride; and T. Curtius and R. Jay, and E. Ebler by boiling benzalazine with hydrochloric acid: $N_2(C_6H_5.CH)_2+2H_2O+2HCl=N_2H_6Cl_2+2C_6H_5.COH$. T. Curtius said that the salt crystallizes from water in octahedra belonging to the cubic system. R. W. G. Wyckoff said that the crystal unit is a cell 7·89 A. in length containing four mols. The structure is said to be like that of the nitrates of the alkaline earths, with hydrazine radicles in place of the metal chlorine atoms in place of the nitrate radicles. The distance between adjacent chlorine atoms is 3·96 A., and between the chlorine and nitrogen atoms, about 3·14 A. H. Schiff and U. Monsacchi found the sp. gr. is 1·4226 at 20°/4°, and they represented the sp. gr., *D*, of aq. soln. containing *w* per cent. of the salt to be $D=0·99826+0·00436w+0·00017w^2$, at 20°. There is therefore a contraction during the dissolution of the salt, and the increase in the contraction is almost proportional to the quantity of salt dissolved. T. Curtius gave 198° for the m.p. of the salt which decomposes at the lower temp.—say, 180°—giving off hydrogen chloride, and forming hydrazine monochloride as a clear glass. If heated rapidly on a hot plate, it decomposes with a hissing noise or maybe with a detonation. If heated for a long time at 140°, it decomposes: $2N_2H_6Cl_2=2NH_4Cl+2HCl+N_2+H_2$. The heats of neutralization, and soln. by M. Berthelot and C. Matignon, and R. Bach, and the mol. refraction by R. Bach were discussed in connection with hydrazine—*vide supra.* E. C. Gilbert found that in the electrometric titration of $0·025M$-soln. of hydrazine sulphate or dihydrochloride with $0·1112N$-NaOH, Fig. 52, there are two inflections corresponding respectively

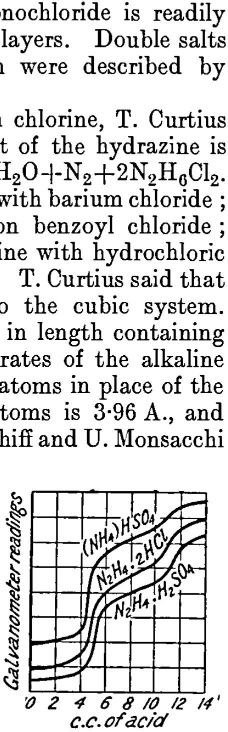


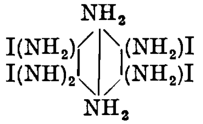
FIG. 52.—Electrometric Titration of Hydrazine Salts with Sodium Hydroxide.

with the first and second eq. of base. This confirms the conclusion of G. Bredig, and R. Bach that the hydrazine salts containing two eq. of acid are largely hydrolyzed in dil. soln., or dissociated into the mono-salt and free acid. The first inflection corresponds with the neutralization of the hydrogen ion thus produced and the second to the formation of the non-ionized base, N_2H_5OH, or $N_2H_6(OH)_2$. The first inflection is sufficiently sharp to indicate that the use of hydrazine in alkalimetry as recommended by R. Stollé is practicable. The result with ammonium hydrosulphate is added for comparison. Each division on the ordinate represents 100 millivolts. According to T. Curtius and co-workers, the dichloride is hygroscopic, readily soluble in water, and sparingly soluble in aq. alcohol. V. H. Veley measured the rate of hydrolysis of hydrazine dichloride. The dry salt was found by E. Ebler to be completely decomposed by dry chlorine at about 100° ; $N_2H_6Cl_2+2Cl_2=6HCl+N_2$—no nitrous oxide was formed; when warmed with bromine water, much gas is evolved, and no solid residue is obtained on evaporation. E. Ebler studied the action of soln. of the dichloride on various salts—stannic, arsenic, molybdic, tungstic, vanadic, platinum, gold, silver, copper, and bismuth. T. Curtius and co-workers, and J. Thiele discussed the action on platinic chloride in alcoholic soln., a yellow precipitate, $(N_2H_5)_2PtCl_6$, is formed, but in aq. soln., the platinic salt is reduced to platinous chloride. K. Seubert and J. Carstens found the velocity of the reduction of chromic anhydride by hydrazine is very fast, and is proportional to the conc. of the chromic anhydride, the hydrazine and the hydrochloric acid present in the soln. The dihalide salts are readily soluble in water, and almost insoluble in alcohol; the monohalide salts are readily soluble in water and warm alcohol; and both are almost insoluble in ether and benzene. The dihalide salts crystallize in the cubic system. According to P. Borissoff, the hydrazine salts are usually isomorphous with the corresponding ammonium salts.

T. Curtius and H. Schulz found that if hydrazine hydrate be allowed to stand over bromine, the base is decomposed, forming nitrogen and hydrogen bromide; but they made **hydrazine monobromide,** N_2H_5Br, as a white crystalline mass, by the action of bromine on hydrazine hydrate suspended in chloroform, or by treating an alcoholic soln. of hydrazine hydrate with hydrobromic acid, and precipitating the salt with ether. The salt can be recrystallized from soln. in warm alcohol. The crystals are anisotropic, and melt at 80°. They also made **hydrazine dibromide,** $N_2H_6Br_2$, by evaporating a soln. of hydrazine hydrate mixed with an excess of hydrobromic acid; by decomposing benzalazine with hydrobromic acid; and by evaporating a mixed soln. of the monobromide and hydrobromic acid. The white powder melts at 195°. The mol. wt. in aq. soln. is only one-fourth the normal value.

T. Curtius and H. Schulz prepared **hydrazine monoiodide,** N_2H_5I, by adding tincture of iodine to a dil. alcoholic soln. of hydrazine hydrate until a point is reached when a drop of the iodine soln. produces a yellow coloration: $5(N_2H_4.H_2O)+2I_2=4N_2H_5I+5H_2O+N_2$. The salt is obtained by evaporation. They also obtained it by evaporating an aq. soln. of hydrazine hydrate and an excess of hydriodic acid; by adding ether to a mixed soln. of hydrazine hydrate and hydriodic acid; and by evaporating a soln. of hydrazine ditritaiodide with an excess of hydriodic acid. The long, colourless, prismatic crystals melt at 127°, and then explode. The mol. wt. of the salt in aq. soln. is half the normal. If the monoiodide be evaporated with an excess of conc. hydriodic acid no **hydrazine diiodide,** $N_2H_6I_2$, is formed; but this salt is produced when benzalazine is treated with fuming hydriodic acid; and, according to R. von Rothenburg, when hydrazine hydrate is treated with methyl iodide. According to T. Curtius and H. Schulz, the product is very hygroscopic, and is coloured brown on exposure to light. It melts at 220°. Its mol. wt. in aq. soln. is one-fourth the normal. R. von Rothenburg found that the diiodide furnishes benzalazine when treated with benzaldehyde; and if hydrazine hydrate be treated with ethyl or isoamyl iodide, **hydrazine ditritaiodide,** $(N_2H_4)_3(HI)_2$, is formed. This salt was previously obtained by T. Curtius and

H. Schulz by adding iodine to a conc. alcoholic soln. of hydrazine hydrate up to the



point at which white crystals are formed. The constitution of the salt is represented by the above graphic formula. The needle-like crystals are optically biaxial; they melt at 90°. The salt is very hygroscopic; and is very soluble in water. The mol. wt. of the salt in aq. soln. is one-fifth the normal—hence the salt dissociates in aq. soln. into three mols of hydrazine hydrate, and two mols of hydrogen iodide. When the aq. soln. is evaporated with hydriodic acid, the monoiodide is formed.

The only evidence of the existence of **hydrazine sulphide** has been discussed in connection with the dissolution of sulphur in hydrazine. The preparation of **hydrazine disulphate,** $N_2H_6SO_4$—generally called *hydrazine sulphate*—has been discussed in connection with the production of hydrazine itself. Its preparation was described by B. P. Orelkin and co-workers. It is produced when a soln. of hydrazine hydrate is crystallized from an excess of sulphuric acid It can be regarded as **hydrazine hydrosulphate,** $N_2H_5.HSO_4$; F. Sommer and K. Weise called it *monohydrazonium sulphate.* It was obtained by T. Curtius, and T. Curtius and R. Jay, in tabular or prismatic crystals which are biaxial. The crystals belong to the rhombic system, and T. Liweh gave for the axial ratios, $a:b:c$ $=0.74532:1:0.82825$; and A. Fock, $0.90117:1:0.60404$. The cleavage is complete. A. P. Sabanéeff found the salt to be isomorphous with hydroxylamine amidosulphate, $NH_2SO_3H.NH_2OH$, and ammonium hydroxylaminomonosulphonate, $NH_4SO_3.NH(OH)$. The sp. gr. is 1·378. T. Curtius and co-workers say that the salt suffers no change at 250°, and that it melts at 254° with the evolution of gas. When melted in a test-tube over the flame, it decomposes explosively into ammonium sulphite, sulphur dioxide, hydrogen sulphide, and much sulphur. The thermal data by R. Bach, and M. Berthelot and C. Matignon are indicated in connection with hydrazine. Fig. 52 shows the result of the electrometric titration of the sulphate with sodium hydroxide. T. Curtius found that the salt is sparingly soluble in cold water, but readily soluble in hot water; T. Curtius and R. Jay said that 100 grms. of water, at 22°, dissolve 3·055 grms. of the salt. The solubility of the disulphate was measured by F. Sommer and K. Weise. Expressing conc., S, in grams of salt per 100 grms. of soln., it was found that in water, Fig. 53,

	20°	25°	30°	40°	50°	60°	70°	80°
S .	2·794	3·302	3·746	4·987	6·538	8·322	10·495	12·580

in sulphuric acid at 25°,

H_2SO_4 .	0	0·4897	4·887	26·59	49·00	116·18	144·18 grms. per litre
S . .	3·302	3·143	2·680	1·541	1·026	0·518	0·4318

in hydrochloric acid at 25°,

HCl .	0	0·3645	3·645	18·25	36·45	66·08 grms. per litre
S . .	3·302	3·156	2·876	2·652	2·639	2·615

and in acetic acid at 25°,

$CH_3.COOH$	0	0·5157	6·8963	33·306	63·00	117·38 grms. per litre
S . .	3·302	3·198	3·147	2·903	2·737	2·323

According to T. Curtius, the disulphate is not dissolved by alcohol. R. Bach reported that the salt in aq. soln. is resolved into the ions $N_2H_5{}^{\cdot}$ and $HSO_4{}'$; T. Curtius and H. Schulz found that the mol. wt. of the salt in aq. soln. is half that of the normal salt; and F. Sommer and K. Weise say that the f.p. measurements correspond with ionization into three ions. According to F. Friedrichs, the salt undergoes a reversible reaction with liquid ammonia, $N_2H_6SO_4 + 2NH_3 \rightleftharpoons (NH_4)_2SO_4 + N_2H_4$—*vide* hydrazine. The disulphate does not react with nor dissolve in liquid sulphur dioxide. Most of the reactions indicated in connection with hydrazine (*q.v.*) were made with hydrazine sulphate. According to F. Sommer and K. Weise, hydrazine disulphate does not yield double salts with other metallic sulphates under ordinary conditions, being largely hydrolyzed into the monosulphate and sulphuric acid. It dissolves in conc. sulphuric acid and deposits colourless crystals of **hydrazine hydrodisulphate,** $N_2H_6SO_4,H_2SO_4$. A definite double salt is obtained by adding the solid sulphate to a hot, concentrated soln. of ammonium sulphate in large excess. Colourless crystals, stable in air but decomposed by water, are obtained having the composition of **ammonium hydrazine disulphate,** $N_2H_6SO_4,(NH_4)_2SO_4$. This is the only known double salt of hydrazine disulphate. P. F. Frankland and R. C. Farmer found that hydrazine sulphate is not attacked or dissolved by liquid nitrogen peroxide.

If a soln. of hydrazine sulphate be exactly neutralized with sulphuric acid, and evaporated, finally in vacuo, crystals of the normal sulphate, **hydrazine monosulphate,** $2N_2H_4.H_2SO_4$, or $(N_2H_5)_2SO_4$, are produced. F. Sommer and K. Weise call it *dihydrazonium sulphate,* and they prepared it by stirring a hot soln. of the ordinary sulphate with an excess of barium carbonate, the reaction being $2N_2H_6SO_4 + BaCO_3 = (N_2H_5)_2SO_4 + BaSO_4 + H_2O + CO_2$. The soln. becomes alkaline, and is then made faintly acid with sulphuric acid and filtered. The filtrate is evaporated and cooled in ice, when a crystalline powder of the **monohydrate** $(N_2H_5)_2SO_4,H_2O$ separates, and may be recrystallized from water, when it forms large, transparent, doubly-refracting, tabular crystals. It is much more soluble in water than ammonium sulphate. The solubility curve, Fig. 53, consists of two branches, intersecting at the transition point between the monohydrate and anhydrous salt, the transition temp. of which is 47·3°. The solubility data expressed in grams of the salt, *S*, per 100 grms. of soln., are as follow :

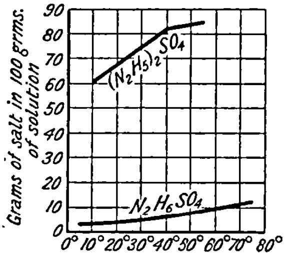


FIG. 53.—The Solubilities of the two Hydrazine Sulphates.

	25°	35°	45°	50°	55°	60°
S	66·91	71·28	78·54	82·33	83·40	84·72

According to C. Montemartini and L. Losana, a 10 per cent. aq. soln. of hydrazine sulphate shows an arrest at 35° and one at 55° on the density-temp. curve. The anhydrous salt forms long, colourless prisms. T. Curtius reported that this salt is deliquescent in air; and is almost insoluble in alcohol. The thermal data by R. Bach have been discussed in connection with hydrazine, $(2N_2,5H_2,S,2O_2,Aq.) = 230·3$ Cals. T. Curtius gave 85° for the m.p.; F. Sommer and K. Weise, 118·9°. L. Longchambon proved that the salt is optically active and gives enantiomorphic crystals; for $\lambda = 436$, 516, and 579, the optical rotations are respectively 4°, 3·05°, and 2·8°. T. Curtius and F. Schrader described double salts of the type $MSO_4.(N_2H_4)_2H_2SO_4$, where M denotes Cu, Fe, Co, Ni, Cd, Zn, and Mn; and F. Sommer and K. Weise assume them to be constituted $M(SO_4.NH_3.NH_2)_2$. They did not succeed in making the double salts with sodium, potassium, or ammonium, but they made the double salt with lithium sulphate, $Li_2SO_4.(N_2H_5)_2SO_4$; calcium sulphate, $CaSO_4(N_2H_5)SO_4$; magnesium sulphate, $MgSO_4.(N_2H_5)_2SO_4.4H_2O$; aluminium sulphate, or *hydrazine-alum,* $(N_2H_5)Al(SO_4)_2.12H_2O$; and chromium sulphate, $(N_2H_5)Cr(SO_4)_2.12H_2O$. When hydrazine sulphate is added to a soln. of nickel sulphate, a reddish-violet precipitate of the trihydrazinate is first obtained, but dissolves to a blue soln., from which blue crystals of a salt, **nickel hydrazinotriaquosulphate,**

$NiSO_4,N_2H_4,3H_2O$, separate after a day. This salt is insoluble and is stable in air, but is decomposed by heating with water.

According to T. Curtius and R. Jay, aq. soln. of hydrazine hydrate attract carbon dioxide from atm. air, and when the soln., sat. with that gas, is evaporated in vacuo, a caustic, syrupy liquid remains—presumably **hydrazine carbonate.** The product is very hygroscopic, sparingly soluble in alcohol, and, according to A. Purgotti and L. Zanichelli, is decomposed by heat.

According to A. P. Sabanéeff and E. Dengin, normal **hydrazine mononitrate,** $N_2H_5NO_3$, was prepared by neutralizing hydrazine hydrate with nitric acid, using litmus as indicator, and crystallizing the liquid. F. Sommer made it by mixing hydrazine disulphate and barium nitrate, adding sodium carbonate to remove free acid, and separating the sodium and hydrazine nitrates by crystallization, fusion at 70°, and recrystallization from methyl alcohol. It is necessary to fuse for some time in vacuo to remove the last traces of alcohol. The salt melts at about 69°; F. Sommer gave 70·71°, and W. R. E. Hodgkinson gave 70°. The last-named said that the salt can be kept for a long time at 100° without change, and that at 200°, in vacuo, it decomposed: $4N_2H_5NO_3=5N_2+2NO+10H_2O$. A. P. Sabanéeff and E. Dengin said that the salt begins to volatilize without decomposition at 140°, and added that it may be heated to nearly 300° without decomposition. It detonates when heated quickly over the free flame. W. R. E. Hodgkinson found that when heated under press., the salt decomposes with explosive violence, but under ordinary press., it burns rapidly. According to F. Sommer, by analogy with ammonium nitrate, hydrazine nitrate, $N_2H_5NO_3$, might be expected to exhibit enantiomorphic inversions, but if such do occur, they have not been detected by thermal, dilatometric, or solubility methods. By cooling from 100°, a labile modification appears at 62°, differing from the stable crystals, but this always changes to the stable form before 40° is reached. The labile crystals melt at 61·8°. A. P. Sabanéeff and E. Dengin found the mononitrate to be very soluble in water; and F. Sommer gave for the solubility, *S*, in grams per 100 grms. of sat. soln.:

	10°	15°	20°	25°	30°	40°	50°	60°
S .	63·63	68·47	72·70	76·61	80·09	85·86	91·18	96·51

The solubility curve is continuous from 10° up to the m.p. A. P. Sabanéeff and E. Dengin said that the mononitrate is very sparingly soluble in absolute alcohol; the hot alcoholic soln. furnishes needle-like crystals on cooling. With conc. sulphuric acid, nitrous oxide is turbulently evolved; dil. sulphuric acid (1 : 1) decomposes the salt, forming hydrazoic acid; and with phosphorus pentachloride, hydrazine monochloride is formed. According to W. R. E. Hodgkinson, the aq. soln. has very little action on metals such as zinc, cadmium, and magnesium, which are strongly acted on by soln. of ammonium nitrate, but the fused salt acts more vigorously than fused ammonium nitrate. Zinc, copper, and most other metals, as well as oxides, sulphides, nitrides, and carbides, cause a flaming decomposition at temp. little above the m.p. Cobalt and nickel that have been thoroughly melted behave like the other metals towards fused hydrazine nitrate, but commercial cubes of cobalt cause a very violent action, followed almost immediately by a severe explosion. Nitrates of bases, such as aniline and toluidine, both in soln. and when fused, behave towards most of the metals in a way analogous to ammonium nitrate.

A. P. Sabanéeff and E. Dengin made **hydrazine dinitrate,** $N_2H_6(NO_3)_2$, by double decomposition with hydrazine disulphate and barium nitrate, or by half neutralizing nitric acid with hydrazine hydrate. On evaporating the soln., needles or plates are formed. The aq. soln. cannot be conc. on the water-bath to more than 30 per cent. nitrate because decomposition then occurs. Alcohol precipitates the mononitrate from the aq. soln. The m.p. is 103°–104° with rapid heating; when slowly heated, it decomposes at 80°–85° without melting, forming hydrazoic acid, nitric acid, nitrogen, water, hydrazine mononitrate, and ammonium nitrate. The salt also decomposes when kept over sulphuric acid at ordinary temp., forming hydrazoic acid, etc.

A. P. Sabanéeff prepared normal or primary **hydrazine phosphate,** or **hydrazine dihydrophosphate,** $N_2H_5.H_2PO_4$, by double decomposition with hydrazine disulphate and barium hydrophosphate; and by neutralization of hydrazine hydrate with phosphoric acid using methyl orange as indicator. The salt is readily soluble in water; it melts without decomposition at about 82°; and its f.p. in water is about half that required to give the normal mol. wt., so that the salt furnishes two ions per mol. It is isomeric with hydroxylamine amidophosphate, $OP(OH)(O.NH_4O)NH_2$. He also made **hydrazine bisdihydrophosphate,** $N_2H_6(H_2PO_4)_2$, by double decomposition with hydrazine disulphate and barium dihydrosulphate; and by dividing a soln. of phosphoric acid in two equal parts, neutralizing one part with hydrazine hydrate, using methyl orange as indicator, and mixing the two soln. Crystals are readily obtained on evaporation. This salt is less soluble than the normal salt. Its f.p. in water indicates the formation of three ions. The salt is isomeric with hydroxylamine amidohypophosphate, $(NH_3OH).H_2P_2O_6$.

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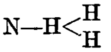
§ 28. Hydrogen Azide, Hydrazoic Acid, or Azoimide

Nitrogen gas is rivalled only by argon and its congeners in its reluctance to take part in chemical changes; but when united with other elements it furnishes a profusion of derivatives remarkable for their great chemical activity. Hence, M. O. Forster[1] could say that nitrogen is one of the most versatile forms of elemental matter. As previously indicated, the extraordinary inertness of ordinary nitrogen, N_2, is attributed to the tenacity with which the two atoms of the mol. remain in combination. In ammonia, and the amines or amides, one nitrogen atom is united with other elements; in hydrazine, the diamides, or diazo-compounds, two nitrogen atoms are grouped together; and in azoimide or hydrazoic acid, or the triazo-compounds, a complex of three nitrogen atoms acts as a monad radicle. The different compounds of hydrogen and nitrogen which have been prepared are as follow:

Bases.		Acid.	Salts.		
NH_3	N_2H_4	N_3H	N_4H_4	N_5H_5	N_7H_9
Ammonia.	Diamide or Hydrazine.	Azoimide or Hydrazoic acid.	Ammonium azide.	Hydrazine azide.	Nitrogen trihydrozinide.

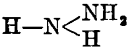
E. J. Maumené[2] claimed to have made a salt of **imide,** or rather **diimide,** NH, or N_2H_2, *i.e.* H—N=N—H, namely, *diimide hydrochloride,* $N_2H_2.2HCl$, by the dry distillation of ammonium chloroplatinate, $(NH_4)_2PtCl_6=4HCl+Pt+N_2H_2.2HCl$, when the salt in question collected in six-sided rhombic crystals, in the neck of the retort. This claim has not been established; T. Curtius and R. Jay did not succeed in making it by heating hydrazine hydrochloride.

While the doubling of ammonia on itself produces diamide or hydrazine, N_2H_4, *i.e.* $H_2=N—N=H_2$, the attempt to extend the operation one stage further, so as to produce N_3H_5, *i.e.* $H_2=N—NH—N=H_2$, **triamide,** or **triazane,** has not been successful.



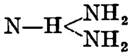
$$N—H<\begin{matrix}H\\H\end{matrix}$$

Ammonia, NH_3.



$$H—N<\begin{matrix}NH_2\\H\end{matrix}$$

Diamide, $NH_2.NH_2$.



$$N—H<\begin{matrix}NH_2\\NH_2\end{matrix}$$

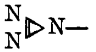
Triamide, $NH_2.NH.NH_2$.

F. Raschig thought that in the reaction between sodium hydroxide and chloramine (*q.v.*), it is probable that there is formed some **triimide,** N_3H_3, or

For sodium triimide, *vide* the action of sodium on hydrazine. The inclination of nitrogen to form long chains and closed rings is far less than is the case with carbon; with the latter, there seems an almost unlimited number of hydrogen compounds; with nitrogen, comparatively few are known, and these are usually unstable bodies, often explosive.

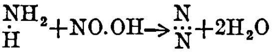
J. Thiele and W. Osborne,[3] and O. Dimroth, however, did succeed in preparing organic derivatives of the open chain triazane or triamide which they named **prozane,** $H_2N.NH.NH_2$, after the well-known hydrocarbon *propane,* $CH_3.CH_2.CH_3$; and H. von Pechmann has prepared organic derivatives of **buzane,** or **tetrazone,** $H_2N.NH.NH.NH_2$, named after the hydrocarbon *butane,* $CH_3.CH_2.CH_2.CH_3$. Still further, T. Curtius prepared organic derivatives of what he called **buzylene,** $NH_2.NH.N:NH$, after the hydrocarbon *butylene,* $CH_3.CH_2.CH:CH_2$; the four-link chains of the nitrogen-hydrogen compounds are sometimes called *tetrazenes* (also *tetrazones*), and both symmetrical $(NH_2.N:N.NH_2)$ and unsymmetrical $(NH_2.NH.N:NH)$ derivatives have been prepared—the former by A. P. N. Franchimont and H. van Erp, and the latter by A. Wohl and H. Schiff. Organic derivatives were also made by E. Fischer, A. Michaelis, A. Angeli, J. R. Bailey, R. Stollé, E. Renouf, etc., and were discussed in the monograph of H. Wieland. Organic derivatives of a chain of five nitrogen atoms $HN:N.NH.N:NH$, *pentazene,* analogous with the di-olefine hydrocarbon *pentadiene,* $CH_2:CH.CH_2.CH:CH_2$, have been made by H. von Pechmann and L. Frobenius. The longest known chain of nitrogen atoms is an eight-link chain in the organic derivatives of **octazone,** $NH:N.NH_2.N:N.NH_2.N:NH$, prepared by A. Wohl and H. Schiff.

When T. Curtius attempted to add another nitrogen atom to the two-linked chain in diamide so as to form a three-linked chain, he found that the two terminal nitrogen atoms linked with one another to form a closed ring of three nitrogen atoms:



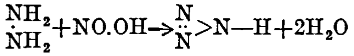
the so-called **triazo-group,** which, in its simplest form, is represented by **hydrazoic acid,** or **azoimide,** N_3H. There is a large class of organic compounds, including many artificial colouring agents, in which the triazo-group is the dominant radicle. The simpler compounds of nitrogen—ammonia, and hydrazine—have basic properties, forming salts with acids, the triazo-hydride has acidic properties, hence the name hydrazoic acid, HN_3. Indeed, it forms with ammonia the curious salt N_4H_4, *i.e.* ammonium azide, $(NH_4)N_3$; and with hydrazine, the still more curious salt N_5H_5—*i.e.* hydrazine azide, $N_2H_4.HN_3$.

When nitrous acid acts on ammonia, say by heating ammonium chloride with sodium nitrite, both atoms of nitrogen are liberated in the form of diatomic mols. The fundamental equation is



$$\begin{array}{l}NH_2\\ \dot{H}\end{array}+NO.OH\rightarrow\begin{array}{c}N\\ \vdots\\ N\end{array}+2H_2O$$

but in 1890, T. Curtius found that if hydrazine be used in place of ammonia, the attack of nitrous acid furnishes the simplest known form of the triazo-group, N_3H. The fundamental equation is



$$\begin{array}{l}NH_2\\ \dot{N}H_2\end{array}+NO.OH\rightarrow\begin{array}{c}N\\ \vdots\\ N\end{array}>N-H+2H_2O$$

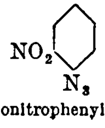
This synthesis of hydrazoic acid, said D. I. Mendeléeff, marks one of the most important achievements of the year 1890. This remarkable acid has no structural parallel among the inorganic acids, and in that respect it occupies an isolated position. The phenyl derivative of this acid, $C_6H_5.N_3$, was discovered by J. P. Griess in 1867.

General usage has not definitely fixed a name for this compound. T. Curtius called it *azoimide ;* H. C. Jones, *triazoic acid ;* L. M. Dennis and co-workers, *hydronitric acid ;* and D. I. Mendeléeff, *hydronitrous acid* The term "azoimide" does not indicate the acid character of the compound, nor the analogy between it and the halogen acids. The term "hydronitric" is presumably intended to indicate the absence of oxygen, and make the name conform with the other hydro-acids. To avoid confusion with the other oxy-nitrogen acids, and to give a hint of the relationship of the acid with the triazo-group, hydrazoic acid is commonly preferred. In any case, the name of the salts should be related with that of the parent acid. L. M. Dennis and co-workers, who used the term *hydronitric acid,* call the salts *trinitrides,* to distinguish them from the ordinary nitrides of the type K_3N, and to keep up the analogy with the halides. E. C. Franklin regarded it as ammoniated nitric acid, and called it *ammononitric acid ;* and A. W. Browne and F. Wilcoxon, in allusion to its formation by the hydrazinolysis of nitrous acid, *hydrazinonitrous acid* or *ammonohydrazonitric acid—vide infra.* If *hydrazoic acid* be applied to this compound, the salts, for the same reason, can be called *azides.* The root of the word "hydrazoic" is of course *azote,* the term used in France for nitrogen.

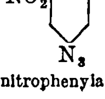
The fundamental reaction just indicated is not well adapted to the production of hydrazoic acid or its salts in quantity. Following L. M. Dennis and co-workers,[4] the methods which have been proposed for the preparation of hydrazoic acid, may be conveniently summarized :

(1) *The action of a compound containing a chain of two nitrogen atoms united to positive atoms or radicles* (e.g. *hydrazine,* $H_2N.NH_2$) *upon a compound containing a single nitrogen atom united to a negative radicle* (e.g. *nitrous acid,* HNO_2).—In the classical experiments of T. Curtius, in conjunction with G. Struve, benzoylazide, $C_6H_5.CO.N_3$, was made by the action of sodium nitrite and acetic acid on benzoylhydrazine, $C_6H_5.CO.NH.NH_2$; and the product was hydrolyzed by a soln. of sodium hydroxide. The resulting sodium azide was mixed with sulphuric acid and distilled to get the hydrazoic acid itself. Sodium ethylate or alcoholic ammonia was later used for the hydrolysis. Hippuryl hydrazine was also found to give better results than benzoyl hydrazine.

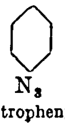
In connection with the hydrolysis of benzoylazide, it is interesting to recall that triazobenzene or phenylazide, $C_6H_5N_4$, is so stable that it cannot be directly hydrolyzed by the action of acids on alkalies to form hydrazoic acid, but E. Nölting and E. Grandmougin were able to show that if an acidic radicle, say a nitro-group, be introduced into the phenyl radicle—say by treatment with nitric acid whereby *p*-nitrophenylazide, $C_6H_4(NO_2)N_3$, is formed—the product is readily hydrolyzed by alkali-lye. Similar remarks apply to the ortho-derivatives, while, curiously enough, the meta-derivatives are not so readily hydrolyzed.



Orthonitrophenylazide.



Metanitrophenylazide.

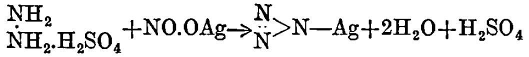


Para-nitrophenylazide.

T. Curtius prepared hydrazoic acid by the action of the red gases evolved from a mixture of nitric acid and arsenic trioxide upon a dil. ice-cold soln. of hydrazine hydrate; and A. Sabanéeff and E. Dengin obtained a 10–12 per cent. yield of hydrazoic acid by heating hydrazine sulphate with nitric acid (sp. gr. 1·3). The formation of hydrazoic acid by heating various hydrazine salts (*q.v.*) was studied by J. W. Turrentine.

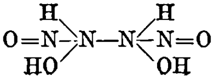
There are many different interpretations of the reaction between hydrazine and nitrous acid since these two substances can furnish a variety of products: for instance, according to A. Angeli: $N_2H_4+HNO_2=N_3H+2H_2O$; M. Dennstedt and W. Göhlich: $3N_2H_4+6HNO_2=2N_3H+2N_2O+O_2+N_2+8H_2O$; J. de Girard and A. de Saporta: $N_2H_4+2HNO_2=N_2+2NOH+2H_2O$; E. Francke: $N_2H_4+HNO_2=NH_3+2NO+H_2O$; H. K. Dey and B. B. Sen: $2N_2H_4+3HNO_2=N_2+2N_2O+NH_3+4H_2O$. F. Sommer and H. Pincas have shown that the reaction is not really so involved as these different equations might suggest if the nature of the soln.—acid or neutral—be taken into consideration. They show that hydrazine and nitrous acid react in neutral soln. to form stable hydrazine nitrite which is decomposed by heat into ammonia and nitrous oxide: (i) $N_2H_4+HNO_2=N_2H_5,NO_2$; and $N_2H_5.NO_2=NH_3+N_2O+H_2O$, a change which is accelerated by the presence of free nitrous acid or other weak acids. With strong acids, the reaction is different: (ii) $N_2H_4+HNO_2=HN_3+2H_2O$ (T. Curtius' reaction); or (iii) $N_3H+HNO_2=N_2+N_2O+H_2O$ (J. Thiele's reaction) in which the hydrazoic acid is destroyed. Hence, in neutral soln., the reactions can be referred to the decomposition of the mols. of hydrazine mononitrite: $N_2H_5NO_2=NH_3+N_2O+H_2O$; and of hydrazine dinitrite: $N_2H_6(NO_2)_2=N_2O+H_2O+NH_4NO_2$ (N_2+2H_2O). J. Thiele's reaction proceeds with a greater velocity than T. Curtius' reaction. Increasing the conc. of the acid favours J. Thiele's reaction and this lowers the yield of hydrazoic acid. The best yield was obtained by using 400 c.c. of a 16·5 per cent. soln. of phosphoric acid, 27·6 grms. of hydrazine chloride, and a soln. of 1·35 grms. of sodium nitrite in 400 c.c. of water. Assuming that this argument is correct, it follows that to obtain a high yield of hydrazoic acid, the conc. of the acid should be high, and the hydrazine conc. low to avoid reaction (i); but if the conc. of the acid be too high, an excess of hydrazine will be needed for protection against reaction (iii). F. Sommer and H. Pincas consider that nitrosohydrazine is an intermediate product of reactions (i) and (ii): $NH_2.NH_2+HO.N:O=NH_2.N:N.OH+H_2O$. The nitrosohydrazine exists in the nitroxyl form, $NH_2.N:N.OH$, and the true nitrosoform $NH(NH_2)NO$. In strong acid soln. the the latter form preponderates and readily breaks down into ammonia and nitrous oxide, whereas in weak acid soln. (*e.g.* acetic acid), an equilibrium may exist leading to both reactions (i) and (ii). The reaction was further discussed by F. Sommer, A. W. Browne and O. R. Overman, and A. Angeli. The last-named assumed that in the formation of hydrazoic acid from hydrazine, an intermediate compound, probably tetrazone, $NH_2.N:N.NH_2$, is formed.

S. M. Tanatar made hydrazoic acid by treating a 3·3 per cent. soln. of nitrogen chloride in benzene with an aq. soln. of hydrazine sulphate. The yield approximated 36 per cent. A. Angeli treated hydrazine sulphate with a cold sat. soln. of silver nitrite when a crystalline precipitate of silver azide was produced in a short time:

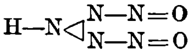


$$\begin{matrix}NH_2\\ \dot{N}H_2.H_2SO_4\end{matrix}+NO.OAg\rightarrow\begin{matrix}N\\ \vdots\\ N\end{matrix}\!>\!N-Ag+2H_2O+H_2SO_4$$

M. Dennstedt and W. Göhlich used potassium nitrite and hydrazine disulphate: $3(N_2H_4.H_2SO_4)+6KNO_2+3H_2SO_4=2N_3H+8H_2O+6KHSO_4+O_2+N_2+2N_2O$. The monosulphate, $(N_2H_4)_2.H_2SO_4$, gives a mixture of ammonia and hydrazine. It is supposed that an unstable hydrazine nitrite, $N_2H_4.2HNO_2$, is first formed with nitrogen quinquevalent:



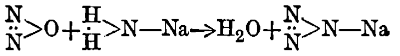
Three mols. of this nitrite condense with the elimination of six mols. of water; and the resulting complex splits into two parts, each of which closes up into a ring with three nitrogen atoms and the simultaneous loss of nitrogen and water to form the intermediate product:



$$H-N\triangleleft\begin{matrix}N-N=O\\N-N=O\end{matrix}$$

which then gives off nitrous oxide and oxygen, leaving hydrazoic acid. J. Thiele obtained better results—in fact, almost a theoretical yield—by using an ethereal soln. of ethyl nitrite and sodium methoxide in well-cooled ethereal soln. R. Stollé used amyl nitrite in place of ethyl nitrite.

2. *The action of a compound containing a chain of two nitrogen atoms united to a negative atom or radicle* (e.g. *nitrous oxide,* N_2O) *upon a compound containing a single nitrogen atom united to positive atoms or radicles* (e.g. *ammonia,* NH_3). The type reaction is $N_2O+NH_3\rightarrow N_3H+H_2O$. W. Wislicenus could not make the acid by the direct union of these two compounds, but was able to make it quite readily from inorganic materials by the action of dry nitrous oxide upon sodamide between 150° and 250°:



$$\begin{matrix}N\\ \vdots\\ N\end{matrix}>O+\begin{matrix}H\\ \vdots\\ H\end{matrix}>N-Na\rightarrow H_2O+\begin{matrix}N\\ \vdots\\ N\end{matrix}>N-Na$$

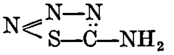
Dry ammonia is passed over metallic sodium in a nickel boat between 250° and 350°, and sodamide, $NaNH_2$, is formed. In about six hours all the sodium will have been converted into amide, and the current of ammonia is replaced by one of nitrous oxide. This is continued at 190° for about 6 hrs. when ammonia is no longer evolved. The product of the reaction is a mixture of sodium hydroxide and sodium azide. This is dissolved in water, the soln. acidified with dil. sulphuric acid (1 : 1), and distilled. The first quarter of the distillation contains most of the hydrazoic acid. W. Wislicenus, and L. M. Dennis and A. W. Browne obtained hydrazoic acid in this way by the ammonolysis of nitrous oxide at high temp., and A. Joannis likewise by working at a low temp. in liquid ammonia. E. C. Franklin obtained sodium azide by allowing a mixture of sodium nitrate and amide to react with liquid ammonia warmed in a sealed tube; and A. W. Browne and F. Wilcoxon, by the action of sodium amide on the fused nitrate: $NaNO_3+3NaNH_2=NaN_3+3NaOH+NH_3$; a 65·7 per cent. yield was obtained at 175°—presumably the high temp. favours the decomposition of the azide. R. Stollé treated cyanamide or dicyanodiamide, or their derivatives, with nitrous oxide at a high temp. in the presence of a catalyst and a dehydrating agent; and distilled the resulting azido-compound with an acid to produce hydrazoic acid.

3. *The simultaneous oxidation of two compounds, one of which contains two nitrogen atoms and the other a single nitrogen atom, and both united to positive atoms or radicles.*—The type reaction: $H_2N.NH_2+NH_2OH+O_2\rightarrow HN_3+3H_2O$, is illustrated by S. M. Tanatar's method in which a hot soln. of mol. proportions of hydroxylamine and hydrazine in dil. sulphuric acid is oxidized by the slow addition of permanganates, bromine, red-lead, lead dioxide, hydrogen dioxide (yield about 26 per cent.), or chromic acid (yield about 29 per cent.). The hydrazoic acid is separated by distillation. L. M. Dennis and co-workers suggest a reversal of this method—the simultaneous reduction of two compounds, one of which contains a chain of two nitrogen atoms and the other a single nitrogen atom and both united to negative radicles—as a likely process for investigation.

4. *The oxidation of hydrazine sulphate by various oxidizing agents.*—The type reaction is symbolized: $3N_2H_4+5O\rightarrow 2HN_3+5H_2O$. A. W. Browne and co-workers made a special study of this process. The fact that ammonia is found among the products of the reaction has led to the inference that there is a side reaction: $2N_2H_4+O_2=N_3H+NH_3+2H_2O$; but F. Sommer has given a more probable explanation of the reaction; he considers that ammonia is the first

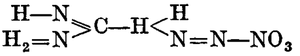
product of the oxidation of hydrazine; and if the oxidizing agent can convert this into nitrous acid, there will be a side-reaction between the nitrous acid and the hydrazine still unacted upon whereby hydrazoic acid is formed, and therefore the formation of hydrazoic acid by the oxidation of hydrazine is a special case of the first type of the methods of preparation here being described. The presence of hydrazoic acid is taken as evidence that nitrous acid was formed as an intermediate product. With *potassium persulphate* as oxidizing agent, A. W. Browne obtained a 40 per cent. yield of the acid; with *hydrogen dioxide* in dil. sulphuric acid, a 28 per cent. yield—the more acid the soln., the greater the yield of hydrazoic acid up to a soln. containing 5 grms. of hydrazine sulphate, 250 c.c. of water, and 100 c.c. of conc. sulphuric acid. *Ammonium metavanadate* at 80° gave a 13·5 per cent. yield; *potassium chlorate*, in the presence of dil. sulphuric acid, 22·4 per cent. of hydrazoic acid accompanied by 48·8 per cent. of ammonia; *potassium bromate*, 6·58 per cent. of hydrazoic acid along with 9·77 per cent. of ammonia; while *potassium iodate* gave no result—the last-named salt, however, does oxidize in the presence of silver sulphate. *Potassium permanganate* and *manganese dioxide*, as oxidizing agents gave respectively 3·2 and 2·3 per cent. of the acid. The production of hydrazoic acid during the electrolysis of hydrazine salts has been discussed in connection with hydrazine.

5. *The decomposition of a compound containing a chain of three or more nitrogen atoms.*—For example, M. Freund and A. Schander prepared hydrazoic acid by the action of alkalies on amidothionitrazole:



$$N\leqslant\begin{array}{l}N{-}N\\ S{-}\ddot{C}{-}NH_2\end{array}$$

and J. Thiele prepared it by the action of alkalies upon diazoguanidine salts, say the nitrate



$$\begin{array}{r}H{-}N\\ H_2{=}N\end{array}\!\geqslant C{-}H{<}\begin{array}{l}H\\ N{=}N{-}NO_3\end{array}$$

The aq. soln. of the free acid can be obtained by distillation with sulphuric acid as indicated above; repeated fractional distillation furnishes a soln. containing 91 per cent. of hydrazoic acid. The remaining water must be removed by calcium chloride.

An aq. soln. of hydrazoic acid was prepared by the Deutsche Gasglühlicht-Auer Gesellschaft by adding oxalic acid and alcohol to a soln. of alkali azide, and removing the precipitate. L. M. Dennis and H. Isham prepared the anhydrous acid by slowly dropping dil. sulphuric acid (2:1) on to dry potassium azide warmed in a large flask, Fig. 54, while a current of air, freed from carbon dioxide and moisture, was passed through the system. The hydrazoic acid is carried by the stream of air through a U-tube with a 30-cm. layer of calcium chloride, and thence into a receiver cooled by liquid air where the hydrazoic acid is frozen to a white solid. To prevent waste, the receiver should be followed by a flask containing methyl alcohol, and fitted with a calcium chloride tube. The apparatus should be placed in a hood behind a screen of thick plate-glass because anhydrous hydrazoic acid is very liable to explode violently at room temp. The hands should be protected by heavy gloves, and the face by a mask with plate-glass goggles. For phosphorus pentoxide as a desiccating agent, *vide infra.*

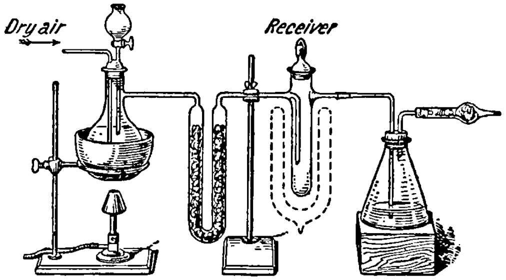


Fig. 54.—L. M. Dennis's Apparatus for Anhydrous Hydrazoic Acid.

The physical properties of hydrazoic acid.—Hydrazoic acid is a colourless, mobile, volatile liquid. According to L. M. Dennis and H. Isham, the liquid is heavier than water and possesses a high surface tension, and large vap. press. At ordinary temp., the liquid appears to be quite stable—a sample kept for 4 or 5 days showed no signs of decomposition. It may be shaken in smooth-walled vessels without danger of explosion. P. J. Kirkby and J. E. Marsh measured the quantity of electricity set free when hydrogen azide is exploded by the passage of an electric spark; they found that the number of ions set free is exceedingly small in comparison with the number of mols. decomposed in the explosion. The ratio was always less than 1 to 100,000, and this seems to indicate that dissociated atoms do not, in general, carry electrostatic charges. It is supposed that the formation of the ions is due to those impacts between the dissociated atoms which occur under specially favourable conditions, amongst which a relatively high velocity is probably the most important. Except under these circumstances, the combination of the dissociated atoms takes place without the production of ions. From experiments at different press. it was found that the hydrazoic acid could not be exploded when the press. was less than about 10 mm. In the case of pure hydrazoic acid this limiting press. would probably be smaller. The value of the limiting press. is much smaller than that obtained in previous experiments with electrolytic gas, for which 80 mm. was observed as the lower limit. After the explosion experiments, copper azoimide was found to be present in the gold-plated brass explosion vessel, and it is shown that this is probably formed in the actual explosion, the dissociated N_3-group being driven through the layer of gold into the brass as a consequence of the forces developed in the mol. disruption. T. Curtius and R. Radenhausen's attempts to determine the vapour density were frustrated by its instability—*i.e.* its explosiveness; but L. M. Dennis and H. Isham succeeded in showing that the vapour density corresponds with the formula HN_3. The liquid boils at 37°, and it furnishes a white solid on cooling. The solid melts at —87°. At the b.p., the liquid vaporizes mainly from the surface, only very small gas bubbles rise through the liquid. It is not decomposed when boiled. According to M. Berthelot and C. Matignon, the heat of formation in aq. soln. is $(3N,H,Aq.)=-61\cdot6$ Cals.; $N_4H_4+Aq.=N_3H.NH_{3soln.}-32\cdot3$ Cals.; $N_4+H_4=N_3H.NH_{3cryst.}-25\cdot3$ Cals. Hydrazoic acid is the most endothermic compound of the nitrogen hydrides. The heat of soln., at 11°, is —7·08 Cals.; the heat of neutralization by baryta, 10·0 Cals., and by ammonia, 8·2 Cals. The heat of combustion at constant vol. is 163·8 Cals., and at constant press., 163·3 Cals. J. C. Philip found that while the increment of at. refraction for an atom of bromine is 8·93, that for the triazo-group is 8·91; and for the at. dispersion, the increment due to bromine 0·35, and to the triazo-group, 0·36. W. Ostwald said that the electrical conductivity of aq. soln. of the acid shows it to be stronger than acetic acid. A. Hantzsch found that the conductivity increases so much with rise of temp. that at 25° the acid is almost as strong as acetic acid, and at 0°, it is rather weaker. C. A. West obtained for the mol. conductivity, μ, for a dilution $v=10$, $\mu=5\cdot38$; for $v=100$, $\mu=15\cdot98$; and for $v=1000$, $\mu=45\cdot97$. The ionization constant thus ranges from $0\cdot0_4166$ to $0\cdot0_4198$; and the value deduced from the inversion of cane-sugar is $0\cdot0_4186$. He therefore inferred that the strength of the acid is somewhat greater than that of acetic acid, and approximately one-seventieth the strength of hydrochloric acid. E. Oliveri-Mandalà gave $0\cdot8\times10^{-5}$ for the ionization constant of the acid for $v=40$ at 0°; $0\cdot9\times10^{-5}$ at 10°; and $1\cdot2\times10^{-5}$ at 20°; and A. Hantzsch gave for $v=64-256$ at 0°, $1\cdot0\times10^{-5}$, and $1\cdot9\times10^{-5}$ at 25°. J. C. Philip, and W. G. Schaposchnikoff studied this question. M. le Blanc found the decomposition potential to be 1·29 volts. E. C. Szarvasy, and A. W. Browne and G. E. F. Lundell showed that during the electrolysis of hydrazoic acid rather a smaller vol. of nitrogen is liberated at the anode than corresponds with theory, and this was attributed to a polymerization of the nitrogen, but A. Peratoner and G. Oddo said that it is more likely to be caused by secondary reactions. According to A. W. Browne and

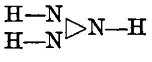
G. E. F. Lundell, purified hydrazoic acid offers a very high resistance to the electric current and has a sp. conductivity approximately equal to that of pure ammonia. On dissolving potassium azide in the anhydrous acid, the conductivity is greatly increased, and when such a soln. is electrolyzed, at —78°, nitrogen and hydrogen are evolved in a ratio which is approximately 3 : 1, but somewhat less under certain conditions. Ammonia is formed during the electrolysis, but hydrazine is not produced. Where the apparatus was not shattered, mercury was attacked at the anode, indicating that active nitrogen is there produced. This subject was studied by F. L. Usher and R. Venkateswaran. L. M. Dennis and H. Isham electrolyzed hydrazoic acid with a zinc anode—*vide infra*, zinc azide. L. Birckenbach and K. Kellermann compared the decomposition potential of the potassium salts of the halogens and what he called the pseudohalogens, and found that they could be arranged in the sequence: TeCy, SeCy, I, SCy, Cy, Br, N_3, Cl, OCy, and F, in which there is no direct relationship between affinity and at. or mol. wt.

The chemical properties of hydrazoic acid.—The resemblances between hydrazoic acid and the halogen hydracids has led some to infer that the triazo-group, N_3, bears a strong family resemblance to the halogens. J. C. Philip found the physical properties—light refraction, light dispersion, boiling point, electrical conductivity, etc.—of the organic triazo-derivatives and the corresponding halogen derivatives to be comparable. In illustration,

	Acetic	Iodo-	Triazo-	Bromo-	Chloroacetic acids.
Ionization constant ($\times 10^{-4}$)	0·01	7·5	9·3	13·8	15·8

In view of the resemblances between the triazo-group and the halogens—*e.g.* Cl—Cl, N_3—Cl, etc.—attempts have been made to prepare a hexatomic nitrogen, N_3—N_3, by linking together two triazo-groups, but with no success other than the naming of the hypothetical $(N_3)_6$, *nitrine*, by L. M. Dennis and A. W. Browne. The analogy between ammonia and water, suggested by E. C. Franklin, led A. W. Browne and T. W. B. Welsh, and H. Goldberg to seek for analogies between the azides and the peroxides.

Work with hydrazoic acid is dangerous because of its poisonous and explosive qualities. The acid has an unpleasant, penetrating odour. According to L. Smith and C. G. L. Wolf, and M. O. Forster, the vapour is extremely poisonous, and, when inhaled in even trifling quantities, causes distressing headache; it is in fact a powerful protoplasmic poison, its activity in this direction being comparable with that of hydrocyanic acid. Its effect on the blood spectrum is immediate and pronounced. O. Löw reported that subcutaneous injections of the sodium salt in certain mammals produce spasms, and symptoms of heart and lung paralysis. The fumes from even dil. aq. soln. were found by T. Curtius and J. Rissom to produce giddiness, headache, and inflammation of the nasal passages. The aq. soln. makes painful burns on the skin. The salts of the alkali metals may be handled without risk of explosion, but those of the heavy metals are dangerously explosive. W. T. Cooke found that hydrazoic acid is partly reduced by sodium amalgam—nascent *hydrogen*—forming ammonia and a little hydrazine; zinc and sulphuric or hydrochloric acid also reduce the acid. Only when the hydrazine is removed, in an insoluble form, from the reacting system, is a considerable quantity of hydrazine produced. It is supposed that the reaction is: $HN_3+3H_2=NH_3+N_2H_4$, and the hydrazine is immediately reduced. No evidence of the formation of *triimide*, or *triazotrihydride*,



$$\begin{matrix} H{-}N \\ H{-}N \end{matrix}\!\triangleright N{-}H$$

was obtained. E. Briner and P. Winkler, and J. Piccard and E. Thomas, studied the reduction of hydrazoic acid. If hydrazine, free from hydrate, be treated with sodium the metal is at first coated with a dark blue layer of, presumably, **sodium hydrazonium** analogous to sodammonium; with the continued action, the liquid becomes yellow. Hydrazoic acid is miscible with *water* or *alcohol*, in all proportions at ordinary temp., without forming any definite hydrate. The aq. soln. is not affected when boiled with water alone. When the aq. soln. is distilled, it seems to form a soln. with a constant b.p. The aq. soln. colours blue litmus red; and in most of its properties its behaviour is comparable with that of hydrochloric acid. As in the case of hydrochloric acid, hydrazoic acid when brought near a bottle of ammonia, furnishes a white cloud of the ammonium salt. Aq. soln.—even very dil.—keep an indefinitely long time in stoppered bottles; but in conc. soln., the acid is dangerously explosive. The acid, said J. Martin, is oxidized in acidic soln. in the presence of ceric sulphate.

F. Raschig found that hydrogen azide exhibits some basic properties, for, with *sodium hypochlorite* and hydrazoic acid, or sodium hypochlorite and sodium azide acidified with acetic or boric acid a highly explosive gas, **chlorazide,** N_3Cl, is formed. This gas smells like hypochlorous acid, and is decomposed by an aq. soln. of sodium hydroxide: $N_3Cl+2NaOH=NaN_3+NaOCl+H_2O$. Chlorazide is slightly soluble in water, forming a yellow soln., and it explodes with extraordinary violence when brought into contact with a flame or glowing splinter, and sometimes spontaneously with the production of a blue flame. K. Gleu found that chlorazide is decomposed at 400° and 2 mm. press. without explosion; the decomposition is accompanied by a red glow, which excites the fluorescence of the glass. The spectrum shows four groups of bands in the red which are attributed to a molecule containing both nitrogen and chlorine; in the ultra-violet, there are continuous bands with maxima at 3060 and 2570 A. This spectrum is not shown by decomposing chlorine dioxide. The addition of hydrogen produces an intense white glow identical with the α-band of ammonia in the visible region. This is attributed to a molecule containing both nitrogen and hydrogen. No nitrogen bands are shown. D. A. Spencer passed dried *bromine* vapour diluted with nitrogen over dried silver or sodium azide, and condensed the product in vessels cooled by a freezing mixture. Violent explosions sometimes occurred. A capillary tube served as a connecting link between the reaction tube and the condensing vessels so as to localize any explosion which might occur. The condensate was fractionated in a current of nitrogen, and **bromazide,** N_3Br, was obtained as a mobile, very volatile, orange-red liquid: $NaN_3+Br_2=NaBr+N_3Br$. Bromazide was also obtained by the interaction of sodium or silver azide and bromine dissolved in ether, benzene, or ligröin. The bromide attacks the solvent to some extent, and it is not possible to separate the solvent from the bromazide. Bromazide is much more volatile than the iodoazide, and likewise much more sensitive to water. A trace of moisture immediately hydrolyzes the compound. The liquid bromazide freezes to a dark red solid at about −45°. The pungent vapour has toxicological properties similar to hydrazoic acid, causing giddiness, headache, and a slackening of the muscles when inhaled. Traces of the vapour irritate the eyes and cause a slight difficulty in breathing, due apparently to congestion of the nasal mucous membrane. Solid, liquid, and vapour are as sensitive to shock as iodoazoimide, the explosion (often apparently spontaneous) being accompanied by a flash of livid blue light. The liquid explodes in contact with phosphorus, arsenic, sodium, and silver foil, but the vapour, when diluted with nitrogen and passed over silver leaf or sodium, gives a film of the corresponding azide and bromide. The liquid is apparently miscible in all proportions with ether, but is less soluble in benzene or ligröin. These soln. are stable for a few hours in the dark, but, when concentrated, are liable to explode on shaking, and on standing gradually decompose, giving nitrogen and bromine, the latter attacking the solvent. When passed into water, bromoazoimide hydrolyzes instantaneously, giving a mixture of hydrazoic and hypobromous acids, and the soln., on standing, evolves nitrogen by interaction of these acids. A trace of ammonium salt is formed during the hydrolysis. When bromoazoimide is passed into potassium iodide soln., iodine is liberated equivalent to the hypobromous acid produced and potassium azide is obtained: $N_3Br+2KI=KN_3+KBr+I_2$. According to A. Hantzsch, silver azide in a cold ethereal soln. of *iodine* gives a yellow explosive and unstable **iodoazide,** $N_3Ag+I_2=N_3I+AgI$. The freshly prepared, aq. soln. of iodoazide is neutral toward litmus and starch, but the soln. soon hydrolyzes into hydrazoic and hypoiodous acids. A trace of ammonia is obtained during the hydrolysis. In non-aqueous solvents, the compound slowly decomposes into iodine and nitrogen. F. Raschig showed that hydrazoic acid is oxidized by a slight excess of iodine and a crystal of sodium thiosulphate, whereby nitrogen is evolved. The gas can be measured and the reaction used analytically. No gas is evolved with a mixture of sodium thiosulphate and iodine, or with hydrazoic acid and iodine. F. Raschig considers that an intermediate compound, $NaIS_2O_3$, is formed: $Na_2S_2O_3+I_2=NaI+NaIS_2O_3$, the intermediate compound readily gives up its iodine to sodium azide or to sodium thiosulphate, forming in the latter case sodium tetrathionate, $Na_2S_2O_3+NaIS_2O_3=Na_2S_4O_6+NaI$. Hence the catalyst $Na_2S_2O_3$ takes up iodine, giving it up to the azide or condenses to tetrathionate. Free mineral acids hinder the reaction, and since sulphuric acid is liberated as a by-product, it is advisable to add sodium acetate. Because of this effect of acids, it is always advisable, too, to keep adding sodium thiosulphate to the soln., and this is best effected by using a crystal about the size of a pea, which takes sufficiently long to dissolve. Hydrazoic acid seems to be the only substance which, whilst unattacked by iodine alone, is oxidized by iodine in the presence of sodium thiosulphate. Bromine water and thiosulphate have the same effect, owing, no doubt, to the formation of $NaBrS_2O_3$. The only other iodine carrier which has been discovered among sulphur compounds is a sulphide. A crystal of sodium sulphide has the same effect, but some sulphur is at the same time set free.

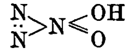
The aq. soln. of hydrazoic acid is slowly decomposed by boiling with dil. *mineral acids.* A. W. Browne and A. B. Hoel found that *hydrochloric acid* heated with a little hydrazoic acid furnishes chlorine: $N_3H+2HCl=NH_3+Cl_2+N_2$; and with *hydriodic acid,* iodine: $N_3H+2HI=NH_3+N_2+I_2$. Just as A. W. Browne and O. R. Overmann found that sulphuric acid deammoniates nitrogen compounds in Kjeldahl's reaction, so sulphuric acid can dehydrazinize the azides, for H. Isham found ammonia and hydrogen in the products obtained by passing dry azomide into conc. sulphuric acid; and H. S. Bennett, by mixing sulphuric acid and an ethereal soln. of azomide. Hydrazoic acid is only slightly oxidized by *potassium chlorate;* while *potassium persulphate* has a marked oxidizing action. W. T. Cooke found *sodium sulphide* reduces hydrazoic acid to ammonia and small quantities of hydrazine.

A. C. Vournazos prepared some complex azides. Anhydrous zinc chloride and sodium azide react in methyl alcohol soln., forming **sodium zinc chloroazide,** $Na[ZnCl_2N_3]$; while with zinc nitrate in aq. soln., **zinc hydroxyazide,** $ZnN_3(OH)$, is formed. Zinc nitrate acts on sodium zinc chloroazide, forming **sodium zinc nitratochloroazide,** $[Zn(NO_3)_2.4ZnCl_2N_3]Na_4.6H_2O$. Similarly, **sodium zinc bromoazide,** $Na[ZnBr_2N_3]$, and **sodium zinc iodoazide,** $Na[ZnI_2N_3]$, were obtained. The iodo-compound reacts with silver iodide to form sodium **silver zinc iodoazide,** $Na(ZnI_2N_3)—AgI—Na(ZnI_2N_3)$; and with lead iodide, **sodium lead zinc iodoazide,** $PbI_2\{(ZnI_2N_3)Na\}_4$. Compounds of sodium zinc azide with hydrocyanic, formic, and acetic acids were also prepared. The action of sodium azide on arsenic tribromide gives **arsenic azide,** $As(N_3)_6$, which reacts with sodium azide, forming the complex **sodium arsenic bromoazide,** $Na_8[AsBr_3(N_3)_8]$. When bismuth iodide is treated with an equimolar part of sodium azide, the reaction is that symbolized: $2BiI_3+2NaN_3+H_2O=BiOI+BiI_3+2HN_3+2NaI$; and with twice this proportion of sodium azide: $BiI_3+2NaN_3+H_2O=BiOI+2NaI+2HN_3$. It is thought that an unstable **bismuth iododiazide,** $BiI(N_3)_2$, is formed and immediately hydrolyzed.

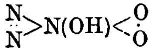
F. Ephraim and H. Piotrowsky obtained evidence of the formation of **hydrazine hydrosulphide,** $N_2H_4.H_2S$, by the action of anhydrous hydrazine on *hydrogen sulphide* (*q.v.*); and there is a possibility that a hydrazinosulphinate (*q.v.*) is formed by the action of hydrazine on thionyl chloride (*q.v.*). F. Raschig said that the reduction of hydrazoic acid with *sodium hydrosulphite* may be represented: $NaHSO_3+NaN_3+H_2O=N_2+NaOH+NH_2.NaSO_3$, together with the subsidiary reaction: $2NaHSO_3+NaN_3+H_2O=Na_2S_2O_6+NH_3+NaOH+N_2$. Just as a secondary amine like diethylamine, $N(C_2H_5)_2N$, reacts with *carbon disulphide* to form the compound $N(C_2H_5)_2.CS.SH$, so F. Sommer found that hydrazoic acid, in the form of an aq. soln. of its sodium salt, reacts with carbon disulphide, at 45°–50°, forming **sodium azidodithiocarbonate,** $N_3.CS.SNa.4H_2O$, in colourless, explosive crystals. The anhydrous salt was also obtained. A. W. Browne and co-workers prepared the dihydrate, as well as **lithium azidodithiocarbonate,** $LiS.CS.N_3.H_2O$; and F. Sommer, **potassium azidodithiocarbonate.** The reactions were also studied by A. W. Browne and A. B. Hoel. They found that potassium azide reacts with iodine in the presence of carbon disulphide, with the formation of potassium iodide and the liberation of nitrogen. The first stage in this reaction consists in the formation of potassium azidodithiocarbonate, $KS.CS.N_3$, by interaction of potassium azide and carbon disulphide, as expressed by the equation $KN_3+CS_2=KS.CS.N_3$. This reaction is irreversible, consequently there is no regeneration of carbon disulphide after it has once reacted. The second stage consists in the reaction between potassium azidodithiocarbonate with iodine, which results in the precipitation of azidocarbon disulphide, $S_2(CS.N_3)_2$, according to the equation $2KS.CS.N_3+2I=S_2(CS.N_3)_2+2KI$. The halogenoid substance azidocarbon disulphide liberates triatomic nitrogen from potassium azide, with resultant evolution of ordinary nitrogen, as shown by the equations $2KN_3+S_2(CS.N_3)_2=2KS.CS.N_3+2N_3$; $2N_3=3N_2$. Combination of these equations with the preceding one leads to the simple expression of the final result obtained when carbon disulphide, potassium azidodithiocarbonate, or azidocarbon disulphide, in relatively small amount, is brought into contact with a soln. containing potassium azide and iodine. These results have been confirmed by iodometric and nitrometric determinations: $2KN_3+2I=2KI+3N_2$. A. W. Browne and co-workers prepared **rubidium azidodithiocarbonate,** $RbS.CS.N_3$, and **cæsium azidodithiocarbonate,** $CsS.CS.N_3$, by the union of carbon disulphide with the alkali azides. The solubilities of the alkali salts decrease in the order Li, Cs, Rb, Na; they are insoluble in carbon disulphide, chloroform, carbon tetrachloride, and benzene. They tend to decompose at the ordinary temp.: $MS.CSN_3=MS.CN+S+N_2$. The violence of the explosion on detonation varies directly as the atomic weight of M, except that the lithium salt is more explosive than the sodium salts. The explosion liberates a gas with a sulphurous odour, leaving a viscous, yellow residue, probably a polymeride of thiocyanogen. The rubidium and cæsium salts are very photosensitive; on alternate illumination and confinement in a dark space, "photolysis" occurs and the salt decomposes. The colour change on illumination is ascribed to free metal atoms held *in situ* in the crystal lattice, their valency electrons having been restored by some photo-process. The salts of the heavy metals—*barium, silver, copper, mercury* (*ic and ous*), *lead, thallium, cadmium, bismuth, and zinc*—are precipitable from soln. of the sodium salt. *Ferric salts* oxidize the compound to *azidothiocarbonyl disulphide,* $(N_3.CS)_2S_2$; many of the azidodithiocarbonates, like the xanthates, are soluble in the ordinary organic solvents, and they do not always show the colour of the metal base. Most of the salts are very explosive. By treating the sodium salt with hydrochloric acid, free **azidodithiocarbonic acid,** $HS.CS.N_3$, is formed. According to G. B. L. Smith, and F. Wilcoxon, this acid has been prepared by the treatment of conc. soln. of the sodium salt with concentrated hydrochloric acid. It is a white or very pale yellow, crystalline solid; it crystallizes in the monoclinic system, has a strong double refraction, and is readily soluble in nonaqueous solvents. It has the characteristic properties of a strong acid, and its strength approaches that of hydrochloric acid. It is easily oxidized by various oxidizing agents, yielding free **azidodithiocarbonate,** $(S.CS.N_3)_2$. In the solid form, the acid is very sensitive to both shock and to heat. It undergoes spontaneous decomposition at the odinary temp., in keeping with the laws of unimolecular change. In the dry state, this reaction is catalyzed by an intermediate product or by the thiocyanic acid formed, but not in aq. soln. The decomposition may be represented by the equation $HS.CS.N_3=HSCN+S+N_2$. The solid product formed consists of polymerized thiocyanic acid and free sulphur. **Ammonium azidodithiocarbonate,** NH_4SCSN_3, was also prepared.

H. E. Rigger studied the f.p. of the system containing **hydrazine** and hydrazoic acid, and obtained as a white, crystalline compound $N_3H.2N_2H_4$, or $N_2H_5.N_3.N_2H_4$, or $N(N_2H_3)_3$, *nitrogen trihydrazinide.* According to J. Thiele, and E. Oliveri-Mandalà, hydrazoic acid reacts with *nitrous acid:* $N_3H+HNO_2=N_2+N_2O+H_2O$. F. Sommer and H. Pincas confirmed this conclusion by adding acetic acid to an eq. mixture of barium nitrate and sodium azide. The reaction can be used to detect nitric acid in the presence of nitrous acid and of nitrous acid alone. Even in a 0·0001*N*-soln., the nitrous acid is destroyed by sodium azide; while nitric acid is not affected by the hydrazoic acid. The reaction was also studied by E. Oliveri-Mandalà, and E. A. Werner. P. J. Kirkby and J. E. Marsh showed that hydrogen azide is readily absorbed by *phosphoric acid,* but no change in vol. occurs when fresh *phosphoric oxide* is used as a desiccating agent. According to E. Oliveri-Mandalà, and T. Passalacqua, when *cyanogen* is passed into a 40 per cent. soln. of hydrazoic acid, **cyanotetrazole,** C_2N_5H, or $C_2N_2.N_3H$, is formed. It melts at 99°, and turns red at 70°. It yields ammonia quantitatively when boiled with potash-lye. It forms **barium cyanotetrazole,** $Ba(C_2N_5)_2Ba.3\frac{1}{2}H_2O$; and **silver cyanotetrazole,** AgC_2N_5. E. Oliveri-Mandalà and F. Noto obtained ethylcarbamazide, $NHC_2H_5.CO.N_3$, from *ethylcarbimide* and hydrazoic acid; **phenylcarbamazide,** $NHC_6H_5.CO.N_3$, from *phenylcarbimide* and hydrazoic acid; and **phenylthiotetrazoline** and a substance, $C_7H_7N_7S$, from *phenylthiocarbimide* and hydrazoic acid respectively at 40° and 60°–70°.

According to T. Curtius and A. Darapsky, a 7 per cent. soln. of the acid acts upon the metals, iron, zinc, cadmium, copper, aluminium, and magnesium, with a brisk evolution of hydrogen and ammonia; a more conc. soln. appears to attack even gold and silver. J. W. Turrentine and R. L. Moore found that when a 2 per cent. soln. of azide is added to finely-divided *copper,* nitrogen is slowly evolved, ammonia is produced, and the metal is gradually changed into cupric azide. The reaction is represented by the equation: $Cu+4N_3H=CuN_6+NH_4N_3+N_2$. F. Raschig found that hydrazoic acid in alkaline soln. is reduced by *aluminium* to hydrazine and ammonia: $HN_3+H_2=N_2+NH_3$; and $HN_3+3H_2=NH_3+N_2H_4$. O. Löw showed that *platinum* black acts catalytically on hydrazoic acid, forming ammonia; and, according to E. Oliveri-Mandalà, the gas liberated during the catalysis of hydrazoic acid by platinum-black consists solely of nitrogen, and estimations of the amounts of this gas and of ammonia formed from a certain quantity of the hydrazoic acid show that the reaction may be expressed by the equation: $3N_3H=4N_2+NH_3$. This final result is probably obtained by way of the intermediate stages $3N_3H=3NH+3N_2$, $3NH=(NH)_3$, and $(NH)_3=NH_3+N_2$. If the catalysis occurs under ordinary conditions, the constant for a unimolecular reaction diminishes very considerably as the reaction proceeds, but if the liquid is stirred to render it uniform and to facilitate the liberation of the gas in the soln., the value of the constant undergoes only very slight alteration. Hydrogen occluded in platinum foil decomposes hydrazoic acid three times as rapidly as does oxygen similarly occluded. Colloidal platinum exhibits only feeble activity in the decomposition of hydrazoic acid in aq. soln., and this result is shown to be due to a "poisoning" of the platinum by the hydrazoic acid; the alkali salts of the latter exert a similar poisoning action on colloidal platinum. J. W. Turrentine and R. L. Moore found that when a 2 per cent. soln. of hydrazoic acid is added to yellow *cuprous oxide,* the latter is rapidly changed to a flocculent substance of darker colour. This substance is an unstable nitrogenous compound (probably cuprous azide), which in contact with excess of hydrazoic acid undergoes gradual transformation into cupric azide. In this reaction the hydrazoic acid suffers reduction with formation of ammonia and nitrogen. The following equation represents this change qualitatively: $Cu_2O+5N_3H=2CuN_6+H_2O+NH_3+N_2$. The transformation takes place more readily in presence of sulphuric acid, and this is probably due to the protective coating of cupric azide being constantly removed by soln. in the acid. The oxidation of cuprous azide by hydrazoic acid is greatly accelerated by light. Again, when *cuprous chloride* is treated with a dil. soln. of hydrazoic acid, it loses its white, crystalline form and becomes bulky, yellow, and flocculent. On addition of hydrochloric acid, the substance resumes its original crystalline form. If cuprous chloride is treated repeatedly with fresh portions of the hydrazoic acid, a substance is produced which resembles that obtained by the interaction of cuprous oxide and hydrazoic acid. This compound is free from chlorine, and appears to be cuprous azide. F. Sommer and H. Pincas found that quadrivalent *cerium salts*—ceric ammonium nitrate, ceric ammonium sulphate, or ceric sulphate—completely oxidize hydrazoic acid in neutral or acid soln. even when very dil.: $2N_3H+2CeO_2=3N_2+Ce_2O_3+H_2O$. It is suggested the reaction can be used analytically by measuring the vol. of the liberated hydrogen provided free hydrochloric acid or chlorides be absent. F. Raschig found that acidic reducing agents like *stannous chloride* and hydriodic acid reduce hydrazoic acid to ammonia and nitrogen. According to A. W. Browne and A. B. Hoel, potassium manganate is formed by the interaction of a heated mixture of potassium azide and *manganese dioxide.* The reaction is vigorous; but hydrazoic acid alone has only a slight action on manganese dioxide. L. M. Dennis and A. W. Browne found that *potassium permanganate* vigorously oxidizes hydrazoic acid to water and nitrogen; some oxygen is liberated at the same time. The action seems to involve a pair of consecutive reactions: $2KMnO_4+10NH_3+3H_2SO_4 \rightarrow K_2SO_4+2MnSO_4+15N_2$ and $2KMnO_4+6NH_3+3H_2SO_4 \rightarrow K_2SO_4+2MnSO_4+6H_2O+O_2+9N_2$, for when the hydrazoic acid is in excess a given amount of permanganate will react with more hydrazoic acid than when the permanganate is in excess. F. Raschig found that hydrazoic acid is not attacked by potassium permanganate in neutral or alkaline soln., but in sulphuric acid soln. it is slowly oxidized to **hypoazoic acid,** N_3OH, thus: $N_3H+O=N_3OH$. In addition, a portion is probably oxidized to triatomic nitrogen which then decomposes. yielding ordinary nitrogen molecules. Hypoazoic acid, N_3OH, resembles hypochlorous acid in many of its properties. It decomposes, yielding oxygen and probably hydrazoic acid. If hydrazoic acid be oxidized in sulphuric acid or boric acid soln. in the presence of sodium nitride, nitric acid is produced in two stages. The two intermediate products are:



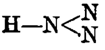
$${}^{N}_{\ddot{N}}\!>\!N\!\leqslant^{OH}_{O}$$



$${}^{N}_{\ddot{N}}\!>\!N(OH)\!<^{O}_{\dot{O}}$$

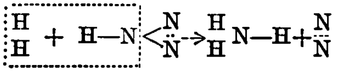
which, losing nitrogen, forms nitric acid. J. Piccard and E. Thomas found that a soln. of **chromous chloride** in acidic soln. reduced hydrazoic acid: $N_3H+H_2=NH_3+N_2$. Hydrazoic acid has only a slight action on *ferric oxide,* but W. T. Cooke found that *ferrous hydroxide* reduces hydrazoic acid, forming ammonia and a very small proportion of hydrazine. For the action of *ferrous and ferric salt* soln., *vide infra.*

The constitution of hydrazoic acid.—The vapour density and analyses both agree that the formula of hydrazoic acid is HN_3. The chief circumstantial evidence in support of the closed ring formula



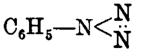
$$H{-}N\!<^{N}_{N}$$

is that it agrees (i) with the formation of hydrazoic acid from sodamide and nitrous oxide; (ii) with the action of hydrogen on thallium azide which results in the formation of nitrogen and ammonia as shown by L. M. Dennis and M. Doan:



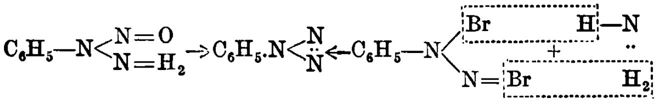
$$\boxed{\begin{matrix}H\\H\end{matrix} + H—N}\!<\!\begin{matrix}N\\ \ddot{N}\end{matrix} \rightarrow \begin{matrix}H\\H\end{matrix}N—H+\begin{matrix}N\\ \vdots\\ N\end{matrix}$$

(iii) with the formation of the potassium salt by the hydrolysis of phenyl azide as indicated above. This suggests that the N_3-group has the same structure in both compounds; and the structure of phenyl azide is assumed to be:



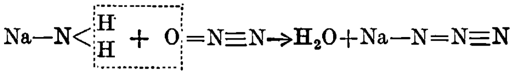
$$C_6H_5—N\!<\!\begin{matrix}N\\ \ddot{N}\end{matrix}$$

as a result of the work of E. Fischer, who showed that the formation of phenyl azide by warming phenylnitrosohydrazine, $C_6H_5.N(NO)NH_2$, with water; and the action of ammonia on diazobenzeneperbromide, $C_6H_5.NBr.NBr_2$, suggest a 3-ring formula for phenyl azide:



$$C_6H_5—N\!<\!\begin{matrix}N=O\\N=H_2\end{matrix} \rightarrow C_6H_5.N\!<\!\begin{matrix}N\\ \ddot{N}\end{matrix} \leftarrow C_6H_5—N\!\begin{matrix}\diagup \boxed{Br \quad H}—N \\ + \quad \ddot{} \\ \diagdown N=\boxed{Br \quad H_2}\end{matrix}$$

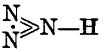
E. Oliveri-Mandalà and F. Noto favoured the ring hypothesis; but the experimental evidence is not so conclusive as to discountenance other interpretations. Metals below magnesium in the electrochemical series reduce hydrazoic acid to ammonia, and maybe to hydrazine and free nitrogen; no hydrogen is evolved, *e.g.* $Cu+3HN_3=CuN_6+N_2+NH_3$; with nitric acid, it will be remembered that $3Cu+8HNO_3=3Cu(NO_3)_2+2NO+4H_2O$. With some of the oxidizable non-metals, the acid is reduced, forming ammonia and nitrogen, thus: $H_2S+HN_3=S+N_2+NH_3$; with nitric acid, $3H_2S+2HNO_3=3S+2NO+4H_2O$; and with metals lying near the end of the electrochemical series, the acid is reduced, forming ammonia and nitrogen: $Pt+2HN_3+4HCl=PtCl_4+2N_2+2H_3N$—with nitric acid under similar conditions: $3Pt+4HNO_3+12HCl=3PtCl_4+4NO+8H_2O$. If two compounds behave in a similar manner, it is often assumed that they have an analogous structure; hence, argued J. W. Turrentine, if nitric acid has the structure $HO—N\equiv O_2$, with a quinquevalent nitrogen atom as nucleus united with two bivalent oxygen atoms, then, hydrazoic acid might be expected to contain a quinquevalent nitrogen atom united with nitrogen, of $H—N=N\equiv N$. He accordingly preferred the alternative term *hydronitric acid* for hydrazoic acid. This view agrees with some reactions in organic chemistry studied by J. Thiele in 1911; and who explained its formation from nitrous oxide and sodamide by assuming that nitrous oxide has the composition $O=N\equiv N$, and, accordingly, he wrote:



$$Na—N\!<\!\boxed{\begin{matrix}H\\H\end{matrix} + O}=N\equiv N \rightarrow H_2O+Na—N=N\equiv N$$

J. W. Turrentine also favoured J. Thiele's hypothesis, and he regarded it as an ammoniated nitrogen nitride in the ammonia system in the same sense that nitric acid is a hydrated nitrogen oxide in the water system, and hence E. C. Franklin called hydrazoic acid *ammononitric acid.* A. W. Browne and co-workers regarded the azides as *pernitrides* analogous to the peroxides when nitric and nitrous acids are intermediate in composition and character between hydrogen pernitride (hydrazoic acid) and hydrogen dioxide. A. W. Browne and F. Wilcoxon said that hydrazoic acid is more closely related to nitrous acid than to nitric acid. Thus, iodine is not liberated by adding one per cent. soln. of nitric acid to hydriodic acid, but it is readily liberated by one per cent. soln. of nitrous or hydrazoic acid. The probable structural similarity of nitrous and hydrazoic acids is indicated by the many methods of preparing hydrazoic acid from nitrous acid or its derivatives. H. E. Armstrong examined the mol. refraction of hydrazoic acid and phenyl azide, but found the evidence did not decide in favour of either the 3-ring formula or the dinitrilic formula $=N-NH-N=$.

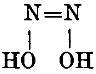
D. I. Mendeléeff argued that just as primary ammonium mesonitrate, $(NH_4O)(HO)_2NO$, is supposed to furnish nitrous oxide by the loss of three mols. of water, so may secondary ammonium mesonitrate, $(NH_4O)_2(HO)NO$, furnish hydrazoic acid by the loss of four mols. of water. This would make hydrazoic acid the nitrile of mesonitric acid :



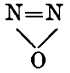
$$\begin{matrix}N\\[-6pt]\cdot\\[-6pt]N\end{matrix}\!\geqslant N-H$$

in the same way that hydrogen cyanide, $H-C=N$, can be regarded as the nitrile of ammonium formate, obtained by the loss of 2 mols. of water. Ammonium azide can be derived from tertiary ammonium mesonitrate, $(NH_4O)_3NO$, by the loss of 4 mols. of water. D. I. Mendeléeff then predicted that the more salient properties of the cyanides (nitriles) would characterize the azides, but subsequent events did not confirm these whimsical speculations. A. W. Browne and F. Wilcoxon add that hydrazoic acid can also be regarded as the nitrile of primary ammonium hyponitrite, $NH_4O.N:N.OH$.

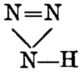
The following graphic formulæ show a kind of relationship between hydrazoic acid, nitrous oxide, and hyponitrous acid :



Hyponitrous acid.



Nitrous oxide.



Hydrazoic acid.

where nitrous oxide appears as if it were the anhydride of hyponitrous acid, and hydrazoic acid as *nitrous imide.* According to W. Schlenk and T. Weichselfelder, when hydrazine is mixed with methyl alcohol, heat is developed, and, on cooling with solid carbon dioxide, a mass of colourless needles is obtained. The mixture has no definite b.p., however, the affinity of hydrazine for alcohol being much smaller than the affinity for water. Hydrazine methylate, $[NH_2.NH_3]OMe$, is isomeric with methylhydrazine hydrate, $[NH_2.NH_2Me]OH$. M. L. Huggins made estimates of the interatomic distances of the atoms in the molecules of the potassium and sodium azides.

Some analytical reactions of hydrazoic acid.—When a ferric chloride soln. or a soln. of iron-alum is mixed with sodium azide ; or when a soln. of ferrous ammonium sulphate is shaken in air with sodium azide, a blood-red coloration is developed. The colour disappears when the liquid is boiled, and ferric hydroxide precipitates, the colour also disappears on standing owing to the separation of a *basic ferric azide—vide supra.* L. M. Dennis and A. W. Browne say that one part by weight of hydrazoic acid per 100,000 parts of water will give a distinct coloration, and hence, T. Curtius and J. Rissom consider this to be a *characteristische Reaktion auf Stickstoffwasserstoff.* The colour persists an indefinitely long time if the ferric salt be in excess—probably because the hydrolysis of the ferric azide is in this way prevented. The red coloration is remarkably like that produced by ferric thiocyanate, but dilute mineral acids, say hydrochloric acid, discharge the colour of the azide, but scarcely affect the colour of the thiocyanate. Mercuric chloride discharges the colour of ferric thiocyanate more readily than it does that of ferric azide. L. M. Dennis recommends the determination of hydrazoic acid and its soluble salts by precipitation as silver azide, *q.v.*, from neutral or acetic acid soln. by the addition of silver nitrate. The precipitate is converted into silver chloride for weighing.

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§ 29. The Azides, Azoimides, Trinitrides, Hydrazoates, or Pernitrides

T. Curtius[1] prepared **hydrazine azide,** $N_2H_4.HN_3$, or H_5N_5, by treating ammonium azide with hydrazine hydrate, or by neutralizing hydrazoic acid with hydrazine hydrate. If a very conc. soln. of hydrazoic acid be treated with hydrazine hydrate until litmus is coloured blue, and the soln. is evaporated over sulphuric acid, or potash, the same salt is formed, and not $N_2H_4.2HN_3$, as might be anticipated by analogies from the behaviour of hydrazine with other acids. Ammonium azide crystallizes in large anisotropic prisms which melt at about 50°. The salt is hygroscopic, and if exposed to air at ordinary temp., it gradually volatilizes—and more readily so in the vapour of water or alcohol. The salt is sparingly soluble in boiling alcohol, and the hot soln., on cooling, deposits tabular crystals. The crystals can be ignited in air, and they burn with a yellow flame and much fuming, without leaving any residue. When rapidly heated in air, say with a white-hot wire, the salt explodes violently; similar explosion occurs with a detonator. The moist salt is also explosive.

T. Curtius prepared **ammonium azide,** $NH_3.HN_3$, or $NH_4.N_3$, or N_4H_4, by passing ammonia gas into an alcoholic soln. of diazohippurylamide, and precipitating the product by the addition of ether. It is also formed from a mixed soln. of hydrazoic acid and ammonia. The salt can be crystallized from its aq. soln. in colourless plates, with habits bearing a formal resemblance to those of ammonium chloride. The crystals are not hygroscopic. The salt is very volatile; even at room temp., T. Curtius and R. Radenhausen said that the crystals volatilize slowly, and in a few days disappear; and the last traces of the salt, with mineral acids, yield hydrazoic acid. The salt fuses at 160°, and at the same temp., it begins to boil and sublime. T. Curtius said that when warmed in a test-tube, sublimation begins at about 100°; if rapidly heated, the salt explodes. Vapour density determinations at 100° gave half the value calculated for N_4H_4, and this corresponded with a complete dissociation of the salt. D. I. Mendeléeff suggested that ammonium azide like ammonium cyanate should undergo an isomeric change when heated, but T. Curtius and R. Radenhausen obtained no evidence of this. M. Berthelot and P. Vieille gave 1350°–1500° for the temp. of the explosion, and they represented the reaction: $2N_4H_4=3N_2+H_2+2NH_3$, and 11–20 per cent. of the ammonia is decomposed. A. R. Hitch found that when heated the salt has a tendency to sublime, and it decomposes into ammonia, nitrogen, and hydrogen. M. Berthelot and C. Matignon gave for the heat of formation: $(4N,4H)=N_4H_4-25{\cdot}3$ Cals., with the solid salt, and $-32{\cdot}3$ Cals. if in soln. R. Bach gave for the heat of neutralization $(NH_3aq.,HN_3aq.)=NH_4.N_3aq.+83$ Cals.; and M. Berthelot and C. Matignon, 8·2 Cals. The heat of soln. is $-7{\cdot}08$ Cals., and R. Bach gave $NH_3.N_3H+Aq.=NH_3.HN_3.Aq.+67{\cdot}34$ Cals. M. Berthelot and C. Matignon found for the heat of combustion, $N_4H_{4\text{cryst.}}+O_2=2N_2+2H_2O+163{\cdot}8$ Cals. at constant vol., and $+163{\cdot}3$ Cals. at constant press. T. Curtius and J. Rissom studied the spectrum of ammonium azide. W. Hittorf found that on electrolysis of the aq. soln., nitrogen was evolved from a platinum anode, and hydrogen and free ammonia from the cathode. A. W. Browne and co-workers found that when a soln. of a gram of ammonium azide in 36 c.c. of liquid ammonia is electrolyzed, copper anodes undergo electrolytic corrosion to an extent indicating the formation of some cuprous azide, CuN_3, with cupric azide, CuN_6, as the main product. No gas was liberated at the anode. With silver, cadmium, lead, and antimony anodes the corrosion resulted in the formation of normal azides, AgN_3, CdN_6, PbN_6, and SbN_9, without liberation of gas at the anode. Aluminium, iron, and nickel anodes undergo corrosion, accompanied by the liberation of nitrogen. The aluminium anode became coated with a bulky pyrophoric scale of varying colour and texture. Deep red ferric azide, FeN_9, was obtained in soln. when an iron anode was employed, but this product was ammonolyzed and yielded an ammono-basic ferric azide. A pink deposit was formed on the nickel anode, presumably an ammono-basic nickel azide. F. Friedrichs, and A. W. Browne and A. E. Houlehan found ammonium azide to be readily soluble in liquid ammonia, and at 110°, the soln. gives two liquid phases; and F. A. Smith measured the conductivity of the soln. F. Friedrichs also found that the azide dissolves in liquid sulphur dioxide, forming two soln. of limited miscibility.

T. Curtius and J. Rissom made **lithium azide,** LiN_3, by the action of a soln. of lithium sulphate on barium azide, and evaporating the clear liquid. The anisotropic crystals were hygroscopic and could not be recrystallized from aq. soln. The salt dissolves in water without the development of heat; the soln. has an alkaline reaction. 100 parts of water at 10° dissolve 36·12 parts of salt; at 15·5°, 62·07 parts; and at 16°, 66·41 parts; again, 100 parts of alcohol dissolve at 16°, 20·26 parts of salt. Lithium azide is insoluble in ether. When the dry or moist salt is heated, decomposition occurs with explosive violence; the decomposition temp. ranges from 115° to 298° according to the rate of heating. L. Wöhler and F. Martin gave 245° for the temp. of detonation of lithium azide. The salt does not explode by percussion. L. M. Dennis and A. W. Browne added that the salt never crystallizes free from water; but always contains a mol of water. L. M. Dennis and C. H. Benedict evaporated a soln. of lithium hydroxide neutralized with hydrazoic acid, in air, and obtained colourless, hygroscopic crystals of **hydrated lithium azide,** $LiN_3.H_2O$, which were readily soluble in water, and soluble in alcohol. L. M. Dennis and C. H. Benedict made **sodium azide,** NaN_3, by evaporating a soln. of sodium hydroxide neutralized with hydrazoic acid; T. Curtius saponified benzoylazide with an alcoholic or aq. soln. of sodium hydroxide; and W. Wislicenus passed a mixture of ammonia and nitrous oxide over molten sodium, or treated sodium amide at 150°–250° with nitrous oxide. According to W. Schlenk and T. Weichselfelder, when thin slices of sodium are gradually added to ordinary free hydrazine in an atm. of pure, dry nitrogen, a colourless precipitate is formed and the liquid develops a yellow colour. The deposit is sodium hydroxide, for the best hydrazine still contains some hydrate. By treating hydrazine in this way until the yellow colour was permanent, and then distilling the hydrazine in a vacuum, the authors have obtained absolute hydrazine, which then dissolved sodium completely with the evolution of ammonia and a little hydrogen. On evaporating the yellow soln., **sodium hydrazide,** $NH_2.NHNa$, remained as a residue of glistening leaflets. It was found to be most violently explosive. A mere breath of air, or a trace of moisture or alcohol, sufficed to produce disastrous results. The preparation of sodium azide was described by B. P. Orelkin and co-workers, and J. Thiele by heating hydrazine hydrate with an aq. soln. of sodium nitrite. According to A. W. Browne and F. Wilcoxon, sodium nitrate is ammonolyzed in contact with fused sodium amide as indicated above. The clear, colourless crystals were found by H. Rosenbusch to be uniaxial hexagonal plates with a strong positive birefringence. According to S. B. Hendrichs and L. Pauling, the X-radiogram of sodium azide agrees with a rhombohedral structural unit containing one NaN_3-mol., and having $\alpha=38°\ 43'$, and $a=5{\cdot}418$ A. L. M. Dennis and C. H. Benedict said the crystals are not hygroscopic; they are not explosive when struck with a hammer; and can be melted without decomposition, but, added T. Curtius and J. Rissom, they detonate at a higher temp. The salt is not decomposed when kept 30 mins. at 350°. E. Tiede gave 330° for the temp. at which sodium azide begins to decompose, in vacuo, and he found that nitrogen came off regularly at 380°. E. Moles gave respectively 300° and 280°. Sodium is deposited on the sides of the reaction vessel. The reaction was also studied by A. R. Hitch. J. A. Cranston and A. Y. Livingstone found the sp. gr. of sodium azide to be 1·846 at 20°; and for the sp. gr. and refractive index of the aq. soln., at 16°,

NaN_3 solution	*N*-	0·5*N*-	0·25*N*-	0·125*N*-
Sp. gr.	0·979	0·954	0·946	0·941
Refractive index	1·371	1·362	1·359	1·351

C. A. West gave for the mol. conductivity of soln. of sodium azide:

v	32	64	128	256	512	1024	2048
μ	100·8	102·9	104·8	105·5	107·2	107·9	107·8

so that $\mu_\infty=10\cdot9$. The rate of increase in the conductivity with rise of temp. is about 2·7 per cent. per degree. J. W. Turrentine studied the electrolysis of 2 per cent. soln. of sodium azide with anodes of various metals. The electrochemical eq. of magnesium is twice as great as would be expected from Faraday's law. Aluminium, zinc, and cadmium also give anode efficiencies of considerably more than 100 per cent. In order to explain these phenomena, it is suggested that the metals dissolve electrochemically at a valency lower than that usually assigned to them with formation of compounds which are readily oxidized. This hypothesis is supported by the fact that reduction products of the N'_3 ion, such as ammonia, hydrazine, and nitrogen, are found in the region of the anode, the presence of which indicates that some reducing agent is formed at the anode. The evolution of nitrogen at the anode was taken to mean that the azide ion was being reduced by magnesium, aluminium, or zinc azides. E. Briner and P. Winkler found that when an alkaline soln. of hydrazoic acid is electrolyzed, nitrogen is liberated at the anode, but the quantity is not the theoretical. A. Peratoner and G. Oddo attribute the deficiency to formation of nitric acid. If the formation of nitric oxide could be proved by the interaction of anodic nitrogen and nascent oxygen, this would furnish an argument in favour of the atomic fixation of nitrogen, the atomic nitrogen coming from the decomposition of the N_3-ion. The formation of nitric acid by the electrolysis of an alkaline soln. of an azide has been confirmed. Such a soln. evolves much free oxygen with the nitrogen, but the amount of nitric acid formed is very small. When a neutral azide soln. was electrolyzed and a stream of oxygen was led into the anodic nitrogen, no nitric oxide was found in the gases, and the amount of nitric acid in soln. was even less than from the alkaline soln. When ozone was used with the oxygen, the nitric acid reaction in the soln. became very distinct. When hydrogen was led into the anode chamber very minute quantities of ammonia were formed, but when an aluminium anode was used, causing the formation of nascent hydrogen by soln. of the metal in the alkaline liquid, ammonia was formed. Only one-third of the nitrogen of the azide is converted into ammonia, the other two-thirds escaping as nitrogen. It may be taken, therefore, that the azoic group decomposes according to the equation $N_3=N_2+N$, giving rise to an atom of nascent hydrogen. J. A. Cranston and A. Y. Livingstone found that the eq. electrical conductivity in methyl alcohol of sp. gr. 0·789 at 20°, is at 25°:

NaN_3 . .	0·1*N*-	0·05*N*-	0·025*N*-	0·0125*N*-
Eq. conductivity .	58·7	69·0	78·8	90·4

T. Curtius observed that sodium azide is insoluble in ether. 100 parts of alcohol at 16° dissolve 0·3153 part of salt; and J. A. Cranston and A. Y. Livingstone found that the solubility of sodium azide in 100 c.c. of solvent, with alcohol of sp. gr. 0·799 at 17°, is 0·22 at 0°, and 0·46 at the b.p. of the soln.; and in benzene at the b.p., it is 0·10. T. Curtius gave for the solubility in 100 parts of water, at 10°, 40·16 parts of salt; at 15·2°, 40·7 parts; and at 17°, 41·7 parts. The dissolution of the salt is attended by a fall of temp., and the soln. has an alkaline reaction. J. A. Cranston and A. Y. Livingstone found the sp. gr. at 20° is 2·056; and for the sp. gr. and refractive index of the aq. soln., at 16°:

KN_3 solution .	0·5*N*-	0·25*N*-	0·125*N*-	0·0625*N*-
Sp. gr. . .	0·956	0·948	0·941	0·938
Refractive index .	1·362	1·360	1·359	1·357

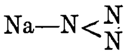
The eq. electrical conductivity in methyl alcohol of sp. gr. 0·789 at 20°, is, at 25°:

KN_3 . . .	0·1*N*-	0·05*N*-	0·025*N*-	0·0125*N*-
Eq. conductivity .	58·7	69·0	78·8	90·4

It will be noted that the solubility of azides of the alkali metals increases as the at. wt. of the alkali metal increases; and that their solubility in alcohol decreases with increasing at. wt. of the alkali metal. J. A. Cranston and A. Y. Livingstone showed that in the presence of platinum black, the alkali azide is decomposed;

$3KN_3+3H_2O=3KOH+4N_2+NH_3$. K. A. and U. Hofmann found that sodium azide reacts with molecular hydrogen and oxygen, forming in the one case $NaNH_2$ with the evolution of nitrogen, and in the other case $NaNO_2$. F. Friedrichs found that sodium azide is readily soluble in liquid ammonia and shows a critical soln. of temp. It is insoluble in liquid sulphur dioxide. According to D. A. Spencer, bromine water reacts instantly with sodium azide soln. to give a mixture of hydrazoic and hypobromous acids, which then interact to produce nitrogen. When the sodium azide is present in quantities larger than are required by the equation: $NaN_3+Br_2+H_2O=NaBr+HN_3+HBrO$, the nitrogen evolution is more rapid owing to the interaction of the hypobromous acid with the excess of sodium azide, and it is for this reason that two equivalents of bromine are able to decompose two equivalents of sodium azide. W. Strecker and L. Claus found that sodium azide reacts with selenium monobromide in the presence of benzene, forming sodium bromide and selenium; and with selenyl chloride, forming nitrogen and $2NaCl.SeO_2.H_2O$. A conc. soln. was found by H. Stamm to give a precipitate with ammonia.

L. M. Dennis and C. H. Benedict made **potassium azide,** KN_3, by evaporating a soln. of potassium hydroxide neutralized with hydrazoic acid. Crystals are readily formed. A slight excess of the acid is desirable. The uniaxial crystals are tetragonal, with the axial ratio $a:c=1:0·57976$. T. Curtius and J. Rissom gave 1 : 0·5810. The optical character is negative, and the crystals are strongly double refracting. S. B. Hendrichs and L. Pauling examined the X-radiogram, and found that the structural unit resembled that of potassium cyanate, being tetragonal with $a=6·094$ A., and $c=7·056$ A., and having four KN_3-mols. per unit cell. According to T. Curtius and J. Rissom, the salt is neither volatile nor hygroscopic. It does not explode when struck with a hammer. When heated, the salt melts and boils; nitrogen is then given off, and the residue inflames with a feeble detonation. It is not changed when heated to 350° in a capillary tube, and at a higher temp., nitrogen is evolved and potassium is formed. E. Tiede found that potassium azide begins to decompose in vacuo at 320°, and nitrogen comes off regularly at 360°. The reaction was also studied by A. R. Hitch—*vide supra*, sodium azide. A. W. Browne and A. B. Hoel used filter-paper impregnated with potassium azide as fuse-paper to detonate silver azide. T. Curtius found that the salt dissolves in water with the production of cold, 100 parts of water at 10·5° dissolve 46·5 parts of salt; at 15·5°, 48·9; and at 17°, 49·6. Again, 100 parts of alcohol dissolve 0·1375 part of salt at 16°; and J. A. Cranston and A. Y. Livingstone found that the solubilities of potassium azide in 100 c.c. of alcohol of sp. gr. 0·799 at 17° are 0·16 at 0°, and 0·54 at the b.p.; with 80 per cent. alcohol at 0°, 1·8, and at the b.p., 5·9; and in benzene at the b.p., it is 0·15. T. Curtius found that the salt is insoluble in ether. The aq. soln. has an alkaline reaction—*vide supra* for the effect of platinum black. According to F. Friedrichs, potassium azide is soluble in liquid ammonia, and shows a critical soln. temp. The salt is only slightly soluble in liquid sulphur dioxide, and at 120°, the salt becomes yellow, and then explodes. According to A. W. Browne and A. B. Hoel, when manganese dioxide is gently heated with potassium azide, the reaction is very violent, and the product leached with water furnishes a green soln. of manganate which soon becomes violet permanganate. J. A. Cranston and A. Y. Livingstone compared the properties of the alkali azides and cyanates and found them to be so much alike that they supposed that the arrangement of the electrons and atoms in the cyanate-ions and azide-ions is the same, and in accord with I. Langmuir's octet theory—**4.** 27, 4—and not respectively:



$$Na{-}N{<}\genfrac{}{}{0pt}{}{N}{N} \qquad\qquad Na{-}O{-}C{\equiv}N$$

T. Curtius and J. Rissom, and L. M. Dennis and C. H. Benedict made the **rubidium azide,** RbN_3, by the methods indicated in connection with lithium azide.

The salt readily crystallizes furnishing plates with the axial ratio $a : c = 1 : 0·5785$. The salt is hygroscopic, and is not decomposed when the aq. soln. is evaporated. The salt is not exploded when struck with a hammer. When heated in a capillary tube, it sinters at 230°, and melts at 330°–340°, and at a higher temp., it leaves a metallic mirror of rubidium, and nitrogen is evolved. E. Tiede found that rubidium azide begins to decompose, in vacuo, at 260°, and nitrogen comes off regularly at 310°. The salt is insoluble in ether; 100 parts of water, at 6°, dissolve 107·1 parts of salt; and at 17°, 114·1 parts; likewise 100 parts of alcohol dissolve 0·182 part of salt at 16°. The aq. soln. reacts alkaline. The aq. soln. has an alkaline reaction. In a similar manner was **cæsium azide,** CsN_3, prepared in small, hygroscopic, uniaxial crystals with a strong, negative, double refraction. The salt does not explode by percussion, and it behaves like potassium azide on a hot plate. It melts in a capillary tube at 310°–318°, and behaves like the rubidium salt at a higher temp. E. Tiede found that cæsium azide begins to decompose, in vacuo, at 290°, and nitrogen comes off regularly at 300°. The salt is insoluble in ether; 100 parts of water at 0° dissolve 224·2 parts of salt; and at 16°, 307·4 parts; while 100 parts of alcohol, at 16°, dissolve 1·0366 parts of salt. The aq. soln. has an alkaline reaction.

L. Wöhler and W. Krupko prepared **cuprous azide,** CuN_3, by gradually adding a soln. of sodium azide to an excess of a conc. soln. of copper sulphite to which potassium sulphite has been previously added followed by acetic acid in quantity just sufficient to dissolve the precipitate formed. The pale greenish-grey cuprous azide inflames at 220°. When exposed to light, it becomes deep red with a violet tinge and furnishes copper and nitrogen. A. W. Browne and co-workers found that cuprous azide is formed by the electrolysis of a soln. of ammonium azide in liquid ammonia, at —67°, using copper anodes. T. Curtius and J. Rissom prepared **cupric azide,** CuN_6—possibly with $\frac{1}{2}H_2O$, or H_2O—by mixing dil. aq. soln. of copper sulphate and sodium azide; washing the precipitate with ice-water, and drying in a desiccator. It was also obtained by the action of 3·87 per cent. hydrazoic acid on copper precipitated by zinc. The product is cupric, not cuprous azide. A. W. Browne and co-workers found that cupric azide is formed by the electrolysis of a soln. of ammonium azide in liquid ammonia, at —67°, using copper anodes. Copper azide is very explosive even when moist, so that it has not been tried for analysis; it is therefore not clear if the salt is anhydrous, hemihydrated, or monohydrated. The brown product consists of anisotropic prisms which are yellow in transmitted light. It is slightly soluble in water, forming a green soln., and boiling water decomposes it slowly with the formation of hydrazoic acid, and copper hydroxide. Cupric azide explodes by friction, even loosening the solid from the filter-paper suffices for the detonation; the explosion by percussion is very violent. A. R. Hitch could not decompose it thermally without explosion. L. Wöhler and F. Martin gave 174° for the temp. of explosion. According to L. Wöhler and W. Krupko, *basic cupric azide,* **cupric oxyazide,** $CuO.CuN_6$, is formed as a yellow hydrated substance when water with normal cupric azide in suspension is heated to 70°–80° in a current of air freed from carbon dioxide until the calculated quantity of hydrazoic acid has been evolved. It inflames at 245°. L. M. Dennis and H. Isham obtained **cupric amminoazide,** $Cu(NH_3)N_3$, by shaking freshly precipitated black cupric hydroxide, while still moist, with an cxcess of hydrazoic acid; and washed the precipitate. A soln. of the precipitate in aq. ammonia deposits crystals of the salt. It explodes when heated or struck. It is insoluble in water, and soluble in dil. acids.

T. Curtius showed that when a dil. soln. of hydrazoic acid is added to silver nitrate soln., **silver azide,** AgN_3, is precipitated quantitatively; indeed, silver nitrate gives a perceptible turbidity with soln. containing one part of acid in a million parts of soln. J. Thiele made the salt by the addition of an ammoniacal soln. of a silver salt to a soln. of diazoguanidine nitrate; the filtrate from the yellow CN_5Ag_3 when treated with dil. nitric acid gave a little silver azide. A. Angeli found that when a cold sat. soln. of silver nitrate is added to a soln. of hydrazine, white needles of silver azide are deposited. A. W. Browne observed that silver azide is formed when a soln. of ammonium azide in liquid ammonia, at —67°, is electrolyzed with a silver anode. T. Curtius showed that when the ammoniacal soln. of silver azide is evaporated, colourless needle-like crystals of the azide are formed; the anisotropic prisms melt at 250°. A. R. Hitch gave 253°–254° for the m.p.; and the azide explodes at about 300° in agreement with L. Wöhler's observation. Nitrogen is given off very slowly at about 251°, and there is a slight ebullition at 253·5°. The salt is very liable to explode, and the detonation produced when a few milligrams is heated or struck, is very violent. L. Wöhler and F. Martin gave 297° for the temp. of detonation. C. A. Taylor and W. H. Rinkenbach studied this subject. A. W. Browne and A. B. Hoel detonated silver azide with fuse-paper impregnated with potassium azide—*vide supra.* The salt is stable in air; but is very sensitive to light, and when insolated, readily decomposes into nitrogen and the metal. L. Wöhler and W. Krupko said that a specimen which had been exposed to light for such a period that decomposition had not occurred beyond the stage corresponding with the possible formation of a subazide, particles of metallic silver were visible under the microscope, and the residue behaved like silver azide when heated or subjected to percussion. L. M. Dennis said that 100 c.c. of boiling water dissolve about 0·01 grm. of silver azide which separates from the cooling soln. in needle-like crystals. T. Curtius said that the salt is virtually insoluble in water and in dil. acids; but unlike silver chloride, added L. M. Dennis, it is fairly soluble in hot dil. nitric acid (1 : 4). D. A. Spencer found that silver azide reacts instantly with bromine water: $2AgN_3+Br_2=2AgBr+3N_2$. The only evidence of the momentary formation of bromazide in aq. soln. is the production of a little hydrazoic acid with the loss of free nitrogen. According to F. Friedrichs, silver azide dissolves in liquid ammonia and the two liquid phases have a critical soln. temp. At about 100°, the mixture becomes explosive. The salt is scarcely soluble in liquid sulphur dioxide, and by raising the temp., the mixture is very explosive. L. M. Dennis and A. W. Browne found silver azide to be decomposed by boiling with dil. sulphuric acid; to be soluble in conc. mineral acids; and to be soluble in aq. ammonia—the ammoniacal soln. can be boiled without reduction. W. Strecker and L. Claus found that silver azide reacts with selenium monobromide suspended in benzene, forming silver bromide and selenium; while selenium tetrabromide forms a pale yellow compound which becomes bluish-black when exposed to light. J. Bekk found that the photographic behaviour of silver azide resembles that of silver chloride and bromide, but its sensitiveness to light is much less than that of the halogen salts. The azide is also much more easily reduced by developing soln., and, in the unripened condition, is characterized by relatively high sensitiveness to the red portion of the spectrum. The first two properties are, in all probability, determined to a large extent by the extreme fineness of the granular structure of the azide. The darkening of silver azide has been shown to be accompanied by the liberation of nitrogen. Although the pure substance is highly explosive, it is found that dried emulsions of silver azide are quite insensitive to shock, and can be manipulated without danger. T. Curtius and J. Rissom added sodium or potassium azide to a soln. of auric chloride, and on evaporating the liquid, obtained needle-like crystals of a **gold azide.** Both the aq. soln. and the dry salt are very liable to explode.

The azides of the alkaline earths were made by T. Curtius and J. Rissom by dissolving the oxides or hydroxides in dil. hydrazoic acid—say 2–8 per cent. The excess of alkaline earth can be removed by passing carbon dioxide into the boiling soln., and the filtrate conc. by evaporation. There remain colourless, rhombic needles of **calcium azide,** CaN_6; and, according to L. M. Dennis and C. H. Benedict, spherical masses of minute crystals may be formed. The crystals are very hygroscopic and deliquescent. T. Curtius found that the salt does not explode by percussion, but it does so if rapidly heated on a metal plate, and it explodes at about 144°–156°

when heated in a capillary tube; when the temp. has attained 120°–130°, metallic calcium appears in the capillary. E. Tiede found that calcium azide begins to decompose, in vacuo, at 100°, and nitrogen comes off regularly at 110°. L. Wöhler and F. Martin gave 158° for the temp. of explosion. T. Curtius and J. Rissom showed that 100 parts of water dissolve 38·1 parts of salt at 0°, and 45·0 parts at 15·2°. The dissolution of the salt results in the cooling of the soln.; the salt is not changed by the evaporation of the aq. soln. 100 parts of alcohol dissolve 0·211 part of salt at 16°. It is insoluble in ether. T. Curtius and J. Rissom prepared **strontium azide,** SrN_6, in a similar way. It is not explosive by percussion and behaves on a hot plate like calcium azide. The glittering plates are hygroscopic. In a capillary tube, it explodes at 194°–195°, and forms metallic strontium at 140°–150°; L. Wöhler and F. Martin gave 169° for the temp. of explosion. E. Tiede found that strontium azide begins to decompose, in vacuo, at 100°, and to give off nitrogen regularly at 140°. A. Petrikaln studied the explosion spectra of the azides of the alkaline earths. T. Curtius and J. Rissom found that 100 parts of water dissolve 45·83 parts of salt, at 16°, and the aq. soln. has an alkaline reaction, but the salt is not changed by evaporation. 100 parts of alcohol dissolve 0·095 part of the salt at 16°; and the salt is insoluble in ether. The salt was also made by L. M. Dennis and C. H. Benedict. M. Berthelot and C. Matignon, and T. Curtius and J. Rissom made **barium azide,** BaN_6, in fine needles or rhombic prisms which, according to H. Rosenbusch, have the axial ratios $a:b:c=0·3424:1:0·8461$. L. M. Dennis and co-workers say that when evaporated over sulphuric acid, crystals of **monohydrated barium azide,** $BaN_6.H_2O$, are formed. T. Curtius and J. Rissom said that barium azide is hygroscopic, and it does not explode by percussion, and behaves on a hot plate like the calcium salt. In a capillary tube, it explodes at 217°–221°, and at about 180°, metallic barium is present. E. Tiede found that, in vacuo, barium azide begins to decompose at 120°, and gives off nitrogen regularly at 160°. A. R. Hitch found that barium azide suffered no change until about 180° was reached when nitrogen was evolved. At 225°, the salt exploded. L. Wöhler and F. Martin gave 152° for the temp. of explosion. According to E. Ebler, barium azide is not decomposed by radium rays. M. Berthelot found the heat of soln. to be 7·8 Cals. T. Curtius and J. Rissom said that 100 parts of water dissolve 12·5 parts of salt at 0°; 16·2 parts at 10·5°; 16·7 parts at 15°; and 17·3 parts at 17°. The solubility of alkaline earth azides in water increases as the at. wt. of the metal increases. 100 parts of alcohol dissolve 0·0172 part of barium azide at 16°. The salt is virtually insoluble in ether. E. Ebler prepared **radium azide**—probably RaN_3—by dissolving the carbonate in aq. hydrazoic acid. The salt was slowly heated in a capillary to 180°–250°, and a shining metallic mirror of elemental radium was formed.

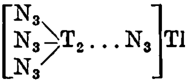
T. Curtius and J. Rissom found that only an impure **beryllium azide** is obtained from a beryllium salt and an azide; they prepared **magnesium azide,** MgN_6, by dissolving magnesium in hydrazoic acid; and by the action of a soln. of magnesium sulphate on barium nitride. The salt explodes when heated. The salt readily dissolves in water; and by boiling with water, the salt loses its explosive qualities. For *magnesious azide, vide supra,* sodium azide. T. Curtius and co-workers dissolved zinc in hydrazoic acid, and observed the evolution of hydrogen with some ammonia, and the formation of anisotropic crystals of a *basic zinc azide,* **zinc hydroxyazide,** possibly $Zn(OH)N_3$. The salt is sparingly soluble in water. W. Wislicenus obtained **zinc azide,** ZnN_6, by the action of nitrous oxide on zinc amide, $Zn(NH_2)_2$, at 150°–250°. L. M. Dennis and H. Isham obtained a soln. of zinc azide in methyl alcohol by the electrolysis of a 6 per cent. soln. of hydrazoic acid in methyl alcohol, using zinc as anode, and platinum as cathode; and, more slowly, by the action of the soln. on zinc in excess. A. Petrikaln studied the explosion spectrum of zinc azide. For *zincous azide, vide supra,* sodium azide. If dry ammonia be passed through the soln. of zinc azide, a white precipitate of **zinc diamminoazide,** $Zn(NH_3)_2N_6$, is produced. Some crystals of the less soluble ammonium azide may be formed. The salt appears in white, acicular crystals, which may be heated without explosion; L. Wöhler and F. Martin gave 289° for the temp. of explosion. The salt is insoluble in water, but in contact with that liquid, the salt becomes opaque, presumably owing to the hydrolytic formation of zinc hydroxide. T. Curtius and J. Rissom obtained **cadmium azide,** CdN_6, by evaporating in a desiccator a soln. of cadmium carbonate in an excess of hydrazoic acid. The salt furnishes tabular crystals which do not explode by percussion. A. W. Browne and co-workers found that cadmium azide is formed when a soln. of ammonium azide in liquid ammonia, at −67°, is electrolyzed with cadmium anodes. L. Wöhler and F. Martin gave 291° for the temp. of explosion. If pyridine be added to an aq. soln. of cadmium azide, a complex *cadmium pyridine azide,* $Cd(C_5H_5N)_2N_6$, is formed.

T. Curtius prepared **mercurous azide,** HgN_3, by treating a soln. of the acid with mercurous nitrate, and M. Berthelot and P. Vieille, by adding a dil. aq. soln. of ammonium azide to mercurous nitrate, and washing the product, first by decantation, and lastly on the filter. The white powder resembles mercurous chloride, and, according to T. Curtius, consists of microscopic, anisotropic needles. It is more sensitive to light than silver azide. When exposed to light, it turns yellow without suffering any other visible change. L. Wöhler said that the yellow colour is produced by the formation of the colloidal metal and nitrogen; the yellow colour passes to orange, brown, black, and finally grey. L. Wöhler and W. Krupko said that unlike mercurous chloride or other mercurous salt, no mercuric azide is formed. T. Curtius said that the azide is less sensitive than lead azide to percussion. According to L. Wöhler, the salt is less explosive than silver azide; and F. Martin made a study of its sensitiveness to explosion. It explodes after some time if kept in darkness and in vacuo at 140°; L. Wöhler and W. Krupko gave 245° as the temp. of detonation; F. Martin, 281°; and L. Wöhler, and F. Martin, 281°. A. R. Hitch found that mercurous azide remains white up to 220°, beyond which it turns yellow, darkens in colour, becoming almost black. It begins to sublime at about 220°; an evolution of gas begins at about 215°, and assumes explosive violence at 270°. F. Martin gave 50·897 Cals. for the heat of detonation. M. Berthelot and P. Vieille gave ±144·6 Cals. for the heat of decomposition. L. Wöhler and W. Krupko said that on percussion the salt immediately decomposes into mercury and nitrogen, and the non-formation of *mercury subazide,* Hg_2N_3, is confirmed by the absence of hydrazoic acid from the products of decomposition of mercurous azide suspended in water. In darkness, the salt may be kept under water for some months without change; the dry salt in vacuo, in darkness, does not change in 24 hrs. at 120°–140°; in gaslight for 24 hrs., the salt becomes pale yellow; and in sunlight it instantly becomes yellow, then dark brown, and black, and finally grey. They found that 100 c.c. of water at ordinary temp. dissolve 0·025 grm. of the salt. T. Curtius said that when treated with dil. aq. ammonia, mercurous azide forms a black insoluble compound. M. Berthelot and P. Vieille obtained **mercuric azide,** HgN_6, by saturating hydrazoic acid with freshly precipitated mercuric oxide. A. Stellbacher prepared mercuric azide as follows:

> A soln. of 6·5 grms. of sodium azide was decomposed with conc. sulphuric acid, and the gaseous hydrogen nitride produced was passed into 10 grms. of mercuric oxide in 200 c.c. of boiling water. The hot soln. of mercuric azide was passed through a filter in a funnel provided with a hot-water jacket, and the filtrate was gently agitated with a wooden splinter during cooling to avoid formation of crystals exceeding 1 mm. in length, these being extremely sensitive. A crystalline mass of mercuric azide was thus obtained of not appreciably greater sensitiveness than silver fulminate. An alternative method consists in mixing conc. soln. of sodium azide and mercuric nitrate; mercuric azide is precipitated from this mixture as a powdery mass, which is even less sensitive than lead azide, but can be converted into the highly sensitive form by solution and crystallization.

The white powder is soluble in hot water; but very sparingly soluble in cold water. On cooling the hot soln., the salt separates in long, white, acicular crystals. The salt is said to be very explosive. A. R. Hitch said that when mercuric azide was heated, gas came off at 212°, and the salt began to boil at 215°; and it exploded at 300°. A. Stettbacher concluded that the extreme sensitiveness of mercuric azide, even under water, renders it unsuitable as a detonating agent. It has the same mol. wt. as mercuric fulminate, and develops the same vol. of gas on detonation, but its *brisance* is twenty times as great. L. Wöhler gave 200°–210° for the temp. of explosion. The salt rapidly becomes yellowish-brown when exposed to sunlight or to ultra-violet rays. L. Wöhler and F. Martin, and C. A. Taylor and W. H. Rinkenbach, studied the influence of the size of grain on the sensitiveness to explosion. L. Wöhler said that no basic mercuric azide is produced when a soln. of hydrazoic acid is warmed with an excess of mercuric oxide, while mercuric azide is not changed when air is passed through water with the salt in suspension.

According to L. M. Dennis, when a soln. of ammonia-alum is treated with an alkali azide, aluminium hydroxide is precipitated, and not *aluminium azide.* For *aluminous azide, vide supra,* sodium azide. T. Curtius and J. Rissom, and L. M. Dennis and co-workers, showed that **thallous azide,** TlN_3, is formed as a white precipitate when ammonium or potassium azide, or hydrazoic acid is added to a soln. of thallous sulphate or nitrate. Thallous azide furnishes transparent, pale yellow tetragonal crystals, which are not hygroscopic. When exposed to light, a thin brown crust forms on the surface—presumably owing to the formation of thallous oxide. The salt is not explosive when heated under ordinary conditions, but when struck with a hammer an explosion occurs. When heated on a hot plate, the salt melts, and boils. Thallium is produced when the salt is heated in a capillary tube. The azide is not altered at 340°, but explodes at a higher temp. L. Wöhler and F. Martin gave 320° for the temp. of explosion. The salt melts at 334°, in an atm. of carbon dioxide, and it is not volatile when heated in nitrogen or hydrogen, the salt is reduced, and in some cases approximately one-third the nitrogen present is converted into ammonia: $N_3H+H_2 \rightarrow N_2+NH_3$. A. R. Hitch said that the salt suffered no change below 330°; at that temp. it melted to a colourless liquid, and it began to sublime at 340°. Nitrogen was evolved at 370°, and an explosion occurred at 430°. Thallous azide is sparingly soluble in cold water, and readily soluble in hot water; 100 c.c. of water at 0° dissolve 0·1712 grm. of the salt; at 5°, 0·1965 grm.; and at 16°, 0·3 grm. The salt in neutral aq. soln. is not altered by evaporation. T. Curtius and J. Rissom added that the spectrum from thallous nitride resembles that from thallous chloride. L. M. Dennis and co-workers found that yellow, needle-like crystals of **thallosothallic azide,** $TlN_3.TlN_9$, are formed when a soln. of freshly precipitated thallic hydroxide in hydrazoic acid is cooled by a freezing mixture. The composition on the co-ordination theory is represented



$$\left[\begin{array}{l}N_3\searrow\\N_3\rightarrow T_2\ldots N_3\\N_3\nearrow\end{array}\right]Tl$$

If the soln. be allowed to crystallize at ordinary temp., *thallic azide,* if it is formed at all, is decomposed with the escape of hydrazoic acid, and the precipitation of thallic hydroxide. Warm water likewise decomposes thallosothallic azide into thallic and thallous hydroxides.

T. Curtius and A. Darapsky prepared a basic salt, **lanthanum hydroxyazide,** $La(OH)(N_3)_2 1\frac{1}{2}H_2O$, by boiling a soln. of lanthanum nitrate and sodium azide. The white, slimy mass of basic lanthanum azide is obtained by evaporating the mixed soln. in vacuo, or by treatment of the soln. with a mixture of alcohol and ether. They also made rose-coloured **didymium hydroxyazide,** $Dy(OH)(N_3)_2$, by evaporating a soln. of didymium carbonate in hydrazoic acid. Freshly precipitated yttrium hydroxide dissolves in hydrazoic acid, forming a soluble *yttrium hydroxyazide;* boiling a soln. of yttrium sulphate and sodium azide gives a precipitate of yttrium hydroxide. L. M. Dennis found that *zirconium hydroxide* is precipitated when a soln. of zirconium salt is treated with potassium azide.

According to T. Curtius and J. Rissom, **tin azide** has been prepared only in a very impure state. A 17 per cent. soln. of hydrazoic acid attacks tin-foil with the evolution of gas and the separation of a white compound which is insoluble in water, and is not explosive. An aq. soln. of stannous chloride gives with sodium azide a precipitate which is thought to be a mixture of stannous azide and hydroxide. It gives off hydrazoic acid when heated with sulphuric acid.

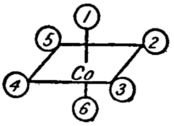
T. Curtius and J. Rissom prepared **lead azide,** PbN_6, by precipitation from a lead salt soln. by hydrazoic acid, or a soln. of ammonium or sodium azide. J. W. Turrentine found a dark brown deposit formed on the lead anodes during the electrolysis of a 30 per cent. soln. of sodium azide; he said that this deposit is probably lead azide, or some other nitride. W. R. Hodgkinson made lead azide by treating hydrazine nitrate with sodium nitrate until the soln. no longer reddens litmus, and then adding lead nitrate soln.; and A. G. Lowndes, by adding lead acetate to a soln. of sodium azide in the presence of sodium nitrate. A. W. Browne and coworkers found that lead azide, PbN_6, is formed when a soln. of ammonium azide in liquid ammonia, at −67°, is electrolyzed with a lead anode. The hot aq. soln., on cooling, furnishes colourless, needle-like crystals which T. Curtius said have only a formal resemblance to those of silver chloride. According to A. G. Lowndes, large crystals are avoided when 0·5 per cent. of dextrine or gelatine is present in soln., and the crystals are smaller if the conc. or the viscosity of the soln. is raised by a non-colloidal addition. Lead azide is very explosive, and it decomposes when warmed. A. R. Hitch said that the salt can be decomposed at 245°–250° without explosion, but it is very liable to explode. The salt decomposes before it melts. L. Wöhler gave 350° for the temp. of explosion; L. Wöhler and F. Martin gave 327°. The explosive properties were also discussed by A. Stettbacher, H. Goldschmidt, F. Martin, W. G. Hudson, C. A. Taylor and W. H. Rinkenbach, and L. Wöhler and W. Krupko. Lead azide can be used in place of mercury fulminate as a detonator for high explosives. L. Wöhler and W. Krupko said that the salt is not changed if kept dry in darkness for 24 hrs. at 115°; but there is a small loss in weight at 170°. Lead azide is extremely sensitive to light; and when exposed to sunlight, it is immediately covered with a dark brown film. From the temp. and percussion tests, it is inferred that the dry salt decomposes into lead and nitrogen when exposed to light. When exposed to air or placed under water, oxidation of the separated lead proceeds simultaneously, and the product consists of lead azide mixed with finely-divided lead hydroxide. The filtrate contains traces of lead, hydrazoic acid, and considerable quantities of ammonia. Reaction thus appears to proceed simultaneously according to the three equations: (i) $PbN_6+2H_2O=Pb(OH)_2+2N_3H$; (ii) PbN_6(in light) $=Pb+3N_2$; (iii) $Pb+N_3H+2H_2O=Pb(OH)_2+N_2+NH_3$. According to T. Curtius, lead azide is insoluble in cold water, but 100 c.c. of boiling water dissolve 0·05 grm. Boiling water slowly decomposes the salt with the formation of a non-explosive lead compound and the expulsion of hydrazoic acid. The salt is insoluble in conc. aq. ammonia; and is easily soluble in hot acetic acid with a gradual decomposition. The freshly precipitated azide is soluble in a soln. of lead acetate. J. W. Turrentine said it is easily dissolved by dil. nitric acid, and slowly, with effervescence by sulphuric acid. W. Strecker and L. Claus found that selenium monobromide reacts with lead azide suspended in benzene, forming lead chloride and selenium.

According to L. Wöhler and W. Krupko, basic lead azide can be prepared in three ways: (i) by heating the calculated quantities of lead azide and lead hydroxide under water in a sealed tube at 140° for twelve to fifteen hours, and separation of the basic azide from specifically heavier unchanged azide by elutriation. The method has the drawback that large, spontaneously explosive crystals of lead azide are liable to separate during the slow cooling of the tube; (ii) by leading a current of carbon dioxide-free air through a boiling aq. suspension of lead azide until the calculated amount of hydrazoic acid has been evolved; and (iii) by heating the requisite quantities of freshly precipitated lead hydroxide and lead azide under water on the water-bath for twenty hours. The two latter methods yield uniform products. The basic azide is less sensitive to percussion or temp. than lead azide, whilst an intimate mixture of lead azide and oxide in the proportions necessary to form the sub-azide shows the same sensitiveness as the pure azide. It is interesting to note that lead azide when mixed with 30 per cent. water has the same sensitiveness as the dry azide, whilst moist mercurous azide is scarcely less sensitive than the dry product.

T. Curtius and A. Darapsky obtained an explosive precipitate by boiling a mixture of cerium nitrate and sodium azide. Freshly precipitated cerium hydroxide dissolves in hydrazoic acid, forming a soln., which, on evaporation, gives a yellow explosive residue **cerium hydroxyazide,** probably $Ce(OH)(N_3)_2$. According to L. M. Dennis, a soln. of potassium azide gives a flocculent precipitate with a neutral soln. of a *thorium* salt: $Th(NO_3)_4+4KN_3+4H_2O \rightarrow Th(OH)_4+4KNO_3+4HN_3$, and L. M. Dennis proposed the reaction for the qualitative detection and quantitative determination of thorium either alone or in the presence of other rare earths. Yttrium, lanthanum, cerium, didymium salts furnish basic azides; uranium, and zirconium are precipitated as hydroxides, and alums behave in the same way. A. W. Browne and co-workers obtained **antimony azide,** SbN_3, using an antimony anode in the electrolysis of a soln. of ammonium azide in liquid ammonia at —67°.

T. Curtius and J. Rissom found that freshly precipitated chromic hydroxide dissolves in hydrazoic acid; and while the soln. of **chromium azide,** $Cr(N_3)_3$, is stable, it decomposes on evaporation, and L. M. Dennis obtained a precipitate of chromium hydroxide by treating a soln. of chrome-alum with potassium azide. E. Oliveri-Mandalà found that a soln. of chromic nitrate treated with 3 mols of sodium azide becomes violet and then green; but nothing separates on standing even with conc. soln. Chromium azide may be separated by means of the insoluble, and stable pyridine compound, **chromium pyridinoazide,** $[Cr(N_3)_3(C_5H_5N)_3]$, or $Cr(N_3)_3.3C_5H_5N$, which forms a green, crystalline crust and explodes violently when heated. When boiled, its conc. aq. soln. deposits mixtures of basic salts of various compositions, **chromium hydroxydiazide,** $OH.Cr(N_3)_2,2H_2O$, which is far less explosive than the original compound, being isolated. Aq. soln. containing chromium azide exhibit the green colour peculiar to complex chromium salts, and do not yield a precipitate with ammonia soln.; even when the experimental conditions are widely varied, addition of silver nitrate does not cause precipitation of the whole of the nitrogen as silver azide. E. Oliveri-Mandalà and G. Comella obtained the normal azide by evaporating the alcoholic soln. in vacuo over potassium hydroxide, and **chromium dihydroxyazide,** $CrN_3(OH)_2$, as a product of hydrolysis. Green crystals of **sodium chromium azide,** $CrN_9.3NaN_3$, were also prepared, and this salt gives a blue coloration with ammonia, and with silver nitrate, it does not form silver azide, but rather a highly explosive complex salt. This indicates that a complex anion is present—probably $[Cr(N_3)_6{}''']$, analogous with $[CrCy_6{}''']$, and $[Cr(SCy)_6{}'']$. The corresponding **chromihydrazoic acid,** $H_3Cr(N_3)_6$, has not been isolated owing, it is supposed, to its ready decomposability. L. M. Dennis obtained a precipitate of uranium hydroxide by treating a soln. of a uranium salt in a similar way. T. Curtius and A. Darapsky found that only a basic **uranium azide** was produced by evaporating a soln. of uranyl hydroxide or potassium uranate in hydrazoic acid.

T. Curtius and J. Rissom showed that the evaporation of a soln. of manganese carbonate in hydrazoic acid gives a pulverulent, non-crystalline **manganese hydroxyazide,** $Mn(OH)(N_3)_2$, which cannot be purified by re-crystallization. The product is sparingly soluble in water; it does not explode by percussion, but does so on a hot plate. L. Wöhler and F. Martin gave 203° for the explosion temp. of manganese azide. T. Curtius and J. Rissom obtained a colourless soln. of **ferrous azide** by the action of sodium azide on a soln. of ferrous ammonium sulphate; when boiled, the salt decomposes; and when shaken in air, a blood-red soln. of **ferric azide** is formed. The same salt can also be obtained directly from ferric salts. When the soln. of ferric azide is boiled, ferric hydroxide is precipitated; and, added T. Curtius and A. Darapsky, if allowed to stand in the cold, a brown **ferric hydroxyazide** is precipitated. A. W. Browne and co-workers obtained ferric azide by the electrolysis of a soln. of ammonium azide in liquid ammonia, at —67°, using an iron anode. L. M. Dennis obtained ferric hydroxide by treating iron-alum with potassium azide—*vide supra,* the analytical reactions of hydrazoic acid. T. Curtius and J. Rissom found that the evaporation of a soln. of cobalt carbonate in hydrazoic acid yields a **cobalt hydroxyazide,** $Co(OH)(N_3)_2$, and some normal **cobalt azide,** $Co(N_3)_2$. When the soln. is treated with potassium azide, crystals of **potassium cobalt azide,** $KCo(N_3)_3$, and with ammonium azide, crystals of **ammonium cobalt azide,** $NH_4Co(N_3)_3$, are formed respectively. L. Wöhler and F. Martin found the explosion temp. of cobalt azide to be 200°. Nickel behaves under similar conditions in an analogous way, furnishing **nickel hydroxyazide,** and **nickel azide,** as well as **potassium nickel azide,** $KNi(N_3)_3$, and **ammonium nickel azide,** $NH_4Ni(N_3)_3$. L. Wöhler and F. Martin found the temp. of explosion of nickel azide to be 200°. A. W. Browne and co-workers obtained nickel azide by the electrolysis of a soln. of ammonium azide in liquid ammonia, at —67°, using a nickel anode. S. Lorie prepared **cobalt diazidotetramminonitrate,** $[Co(NH_3)_4(N_3)_2]NO_3+H_2O$, by the action of sodium azide on cobalt dinitratotetramminonitrate; **cobalt diazotetramminoiodide,** $[Co(NH_3)_4(N_3)_2]I+H_2O$, by the action of potassium iodide on the corresponding nitrate; and **cobalt diazotetrammino-dithionate,** $[Co(NH_3)_4(N_3)_2]S_2O_6+H_2O$, by the action of sodium dithionate on the nitrate. Remembering that the symbol "En" is used for ethylencdiamine, $NH_2.CH_2.CH_2.NH_2$, and that the positions of the radicles in the ammino-compounds are numbered in accord with the appended scheme:



S. Lorie reported **cobalt 1 : 2-dichlorobisethylenediamineazide,** $[Co(En)_2Cl_2]N_3$, to be formed by the action of sodium azide on 1 : 2 cobalt dichlorodiethylenediamine-chloride; **cobalt 1 : 6-dichlorobisethylenediamineazide,** $[Co(En)_2Cl_2]N_3$, by the action of sodium azide on the corresponding chloride; **cobalt 1 : 6-diazidobis-ethyleneamineazide,** $[Co(En)_2(N_3)_2]N_3$, by the action of sodium azide on the corresponding dichlorodiethylenediamine-chloride; **cobalt 1 : 6-diazidobisethylene-diamine thiocyanate,** $[Co(En)_2(N_3)_2]CNS$, by the action of potassium thiocyanate on the azide; **cobalt 1 : 6-diazidobisethylenediaminedithionate,** $[Co(En)_2(N_3)_2]S_2O_6$, by the action of sodium dithionate; **cobalt 1 : 6-diazidobisethylenediaminenitrate,** $[Co(En)_2(N_3)_2]NO_3$, by the action of sodium nitrate; **cobalt 1: 6-diazidobisethylene-diaminechloroaurate,** $[Co(En)_2(N_3)_2]AuCl_4$, by the action of hydrochloroauric acid on cobalt 1 : 6-diazidodiethylenediamine azide; and **cobalt 1 : 6-diazidobis-ethylenediaminechloroplatinate** by the action of hydrochloroplatinic acid on cobalt 1 : 6 diazidoiethylenediamine azide.

T. Curtius and J. Rissom mixed a conc. aq. soln. of hydrochloroplatinic acid and potassium azide in the molar proportions 1 : 2, and on evaporation of the red soln. obtained a residue which exploded with *ein fruchtbarer Detonation,* and doubtless contained *platinum azide.* When the proportions of the original constituents were in proportions conformable with $H_2PtCl_6+8N_3K=K_2Pt(N_3)_6+2N_3H+6KCl$, what appeared to be potassium azidoplatinate was formed. On evaporation, the conc. aq. soln. exploded. By mixing ammonium azide and hydrochloroplatinic acid, and concentrating the soln. by evaporation, a very explosive residue was obtained.

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§ 30. The Fixation of Atmospheric Nitrogen by Organisms

The fertility of cultivated fields and gardens is dependent upon the amount of combined nitrogen which is added as manure or fertilizer. Of course, cultivated plants require fertilizers containing other elements—phosphorus, potassium, etc.—but the problem of supplying available nitrogen is predominant. This has long been recognized. Thus, about the middle of the seventeenth century, J. R. Glauber [1] wrote :

> Deservedly may saltpetre or nitre be termed the universal subject and wonder of the world. . . . If it were not so, how comes it to be so plentifully found in all things ? . . . All these things which dung the fields and lands, and fatten them most necessarily contain in them saltpetre ; for, from this only and alone, comes all the fertility throughout the whole earth, which axiom cannot be gainsayed. . . . Having shown that nitre or saltpetre may be had from all things, *viz.*, from herbs, wood, four-footed beasts and creeping things, from birds in the air, and fishes in the water, yea, from the very elements themselves—earth, water, air, and fire—it must needs follow that it is that so much spoken of universal spirit, without which nothing can either be or live. It is the begetter and destroyer of all things, as I have demonstrated in my *Miraculum mundi* out of the most ancient philosopher Hermes. I therefore hope that nobody will any more doubt thereof or oppose himself with a perverse stubbornness against a truth so manifestly known. . . . If any one is minded firmly to cleave to his own stubborn perverseness, even Hermes himself, should he rise from the dead, would lose his labour in teaching him.

A. L. Lavoisier demonstrated that nitric acid does not pre-exist in the chalk of Roche Guyon, and Mousseaux, but is formed by the action of air. In 1796, W. Saltonstall inferred that at the instant of its escape from putrefying substances, nitrogen is oxidized by the oxygen of the air ; and P. Thouvenel produced nitrates by exposing chalk to the gases evolved from the putrefaction of animal and vegetable substances—mixtures of ammonia and air ; and he concluded :

It is demonstrated by our experiments that atmospheric air possesses all that is necessary to serve for nitrification, as well as air which emanates from putrescent bodies provided it finds matter capable of absorbing the materials.

Early in the nineteenth century the deposits of nitrates in the Peruvian desert attracted attention, and the subject was discussed by J. B. J. D. Boussingault, M. Longchamp, T. Graham, J. L. Gay Lussac, etc.—*vide*, 2. 20, 36. It was soon recognized—*e.g.* by H. Davy, J. von Liebig, J. B. J. D. Boussingault, and G. J. Mulder—that the production of nitrates in soils is at the cost of the organic nitrogen which is present. The nitrogen contained in soils is made up of ammonia, nitrates, nitrites, and mainly organic compounds. The organic matter is largely derived from the tissues of plants and animals, and is often referred to as humus. According to S. L. Iodidi, humus consists largely of proteins together with their decomposition products. There are also nucleoproteids, and non-protein substances like acid amides, and amino-acids. Under the influence of proteolytic enzymes, bacteria, or chemical agents, the proteins are decomposed first, forming allumoses, peptones, and polypeptides, and then mono- and di-amino-acids, and acid amides ; and the nucleoproteids furnish nucleins, nucleic acid, and purine and pyrimidine bases, as well as some proteins.

C. F. Schönbein thought that the nitrates in soils were produced by the union of atm. nitrogen with evaporating water to form ammonium nitrite—*vide supra*, ammonia. G. J. Mulder, S. de Luca, S. W. Johnson, and A. Houzeau attributed the nitrates to the action of ozone on the nitrogen associated with organic matter. F. Goppelsröder, and L. Carius assumed that nitrates are formed by electrical discharge in air. C. P. Collard de Martigny believed that the bases present in soils exerted a predisposing affinity on the nitrogen whereby nitrates were formed. F. A. Haarstick assumed that the iron oxides in soils stimulated the formation of nitrates ; and, according to N. A. E. Millon, the slow oxidation of alkali ulmates in the soil induces the oxidation of ammonia by contact action. N. A. E. Millon, and also F. H. Storer found that all attempts to oxidize ammonia in the wet way by ferric oxide have proved unavailing. A. Müntz and T. Schlösing first demonstrated that the nitrification in soils is the work of organized ferments, or bacteria. The production of nitrates can be arrested by raising the temp. to 100°, or by treatment with chloroform, which has but little effect on soluble ferments. R. Warington also showed that antiseptics like carbon disulphide, and phenol, as well as chloroform, are inimical to nitrification ; that where nitrification has been arrested, that process can be restarted by seeding with a substance already nitrifying ; and that light hinders the activity of the organism responsible for the oxidation of ammonia. These results were confirmed by P. P. Deherain, E. M. Davy, J. H. M. Munro, and E. Godlewsky. The biological character of the nitrification process was indicated by the work of A. Müller, J. Soyka, etc. A. Müntz and T. Schlösing isolated the bacterium—*micrococcus nitrificans*—thought to be responsible for the nitrification of ammonia in soils. R. Warington then showed that the nitrification is really the joint effect of two organisms; one converts ammonium salts into nitrites, but fails to change nitrites into nitrates even after the lapse of several years. The subsequent conversion of nitrites to nitrates is the work of another organism, although, as A. Müntz showed, the nitrites may be oxidized chemically by the joint action of the carbon dioxide and oxygen of the atm. P. F. and G. C. Frankland isolated the bacillococcus which produces nitrous acid from ammonium salts; and S. Winogradsky, the bacterium which transforms the nitrites to nitrates, but has no action on ammonium salts ; and also the one which converts ammonium salts to nitrites. W. Omeliansky failed to detect the presence of an oxydase secreted by the organism which oxidizes ammonia to nitrite either in the filtered medium or in the disintegrated bacteria. The organism which oxidizes nitrites to nitrates cannot oxidize sulphites to sulphates, or phosphites to phosphates.

S. Winogradsky emphasized the ubiquitous distribution of the bacteria concerned with nitrification; he found them in the soils of all climates; in sea-waters; in drainage waters; etc. This has also been confirmed by A. Müntz, F. Weis, P. Ehrenberg, W. Migula, A. Beddies, H. Schultz-Schultzenstein, H. S. Fremlin, F. L. Stevens and W. A. Withers, K. F. Kellermann and T. R. Robinson, A. D. Hall, H. V. von Falckenstein, P. Thomsen, K. Brandt, E. Baur, E. E. Reid, F. Diénert, G. G. Nasmith and G. P. McKay, P. Rudnik, etc. According to A. Müntz and E. Lainé, the filtration of dil. ammoniacal soln. through animal charcoal or peat is accompanied by some nitrification. F. Hüppe, W. Heraeus, R. Warington, A. Müntz, T. Leone and O. Magnanini, T. Schlösing, M. Berthelot, P. F. and G. C. Frankland, E. Chuard, O. Helm, A. D. Hall, W. Omeliansky, P. P. Dehérain, and J. Wortmann showed the dual nature of the process, for the bacteria assimilate not only nitrogen but also carbon from dil. soln. of ammonium carbonate. The work of R. Roche, St. von Bazarewsky, and G. G. A. Weber showed that the most favourable temp. for nitrification by bacteria is 25°–27°. St. von Bazarewsky, A. Koch, J. G. MacBeth and N. R. Smith, P. P. Dehérain, T. Schlosing, H. Buhlert, P. Mazé, T. L. Lyon and co-workers, and W. P. Kelley found that the nitrification process is most active near the surface of the soil, and the aeration of the soil favours the process. The presence of about 17·5 per cent. of moisture was found by A. E. Traaen, A. P. Lipman and co-workers, O. Lemmermann, R. Stewart and J. E. Greaves, J. C. MacBeth and N. R. Smith, R. Roche, W. Buddin, and W. P. Kelley to be most favourable for the nitrification, but the nature of the soil is also of influence. Other things being equal, highly acidified soils were found by E. E. Ewell and H. W. Wiley, and P. L. Lyon and J. A. Bizzell to be harmful, while basic soils are beneficial. E. Murmann, S. Machida, P. E. Müller and F. Weis, H. Fischer, J. Vogel, O. Lemmermann and co-workers, E. B. Fred, E. Polszeniusz, W. A. Withers and G. S. Fraps, W. P. Kelley, F. Miller, and T. Arnd found calcium carbonate favours nitrification, but not so magnesium carbonate; S. Dezani, and J. W. Paterson also found gypsum favourable, but not to the extent of calcium carbonate. J. G. Lipman, J. Crochetelle and J. Dumont, found sodium carbonate harmful, sodium chloride less so, and sodium sulphate still less so. P. L. Gainey, C. de Briailles, and A. Pagnoul found carbon disulphide to be harmful; and P. Cacciari, that naphthalene is also harmful; while A. Koch and A. Oelsner observed no ill-effects with tannin or pine resin. J. E. Greaves noted that arsenic stimulated the activity of the bacteria, and C. Montanari, and G. Leoncini, likewise salts of manganese and of the heavy metals. S. Winogradsky, W. Omeliansky, and O. Meyerhof found that relatively small proportions of glucose, peptone, asparagin, glycerol, urea, sodium acetate, sodium butyrate, and ammonia act deleteriously on both the nitrite and nitrate ferments. J. G. Lipman and P. E. Brown found nitrification dependent on the conc. of the ammonium salts present; R. Perotti, that the speed of nitrification follows a logarithmic curve; and W. Omeliansky, and O. Meyerhof, that a high conc. of ammonia or of nitrite is harmful; the optimum conc. of the nitrite is about 0·05 per cent. with a second optimum with 0·1 per cent.—over 0·3 per cent. interferes with the progress. E. Rolants observed that 0·2 grm. of free ammonia per litre is completely nitrified; but with 0·5 grm. per litre, the process is inhibited, and E. Boullanger and L. Massol, that the process is at a standstill with 30–50 grms. of ammonium carbonate per litre, but works well with 2 grms. per litre. Attempts have been made by A. Müntz and E. Lainé, E. Boullanger and co-workers, H. L. R. Lunden and C. T. Thorssell, and others to utilize the bacterial oxidation of ammonia to nitrates; but the reactions are so slow, the space required for handling the enormous bulk of dil. soln. required is so large; and the cost of evaporating these dil. soln. is so great that the results on an industrial scale are not likely to be profitable. For the denitrification of nitrates by bacteria, *vide* the formation of nitrogen, ammonia, and nitrites. F. Löhnis has discussed the nitrification and denitrification of soils. According to P. Haupt, and A. Tschirch, the absorption of atm. nitrogen by leguminous plants is due to electronic action, and this view was supported by the work of E. Hiedemann, and F. Fichter and R. Suter. D. Burk discussed the free energy of the fixation of nitrogen by living organisms.

J. B. J. D. Boussingault tried if certain fungi—*e.g.* the *penicillium*—can fix atm. nitrogen, but the results were negative. On the other hand, F. Sestini and G. del Torre, J. G. Lipman, W. P. Latham, E. I. Fulmer and L. M. Christensen, C. Ternetz, K. Puriewitsch, and K. Saida obtained positive results. Numerous investigations have been made on this subject. H. Davy said that the earthy constituents of soils are alone unable to fix the nitrogen as plant food. M. Berthelot, however, was able to prove that the bacteria in soils are able to enrich the soil by fixing atm. nitrogen. This result was confirmed by the work of P. P. Déhérain and L. Maquenne, E. J. A. Gautier and R. Drouin, T. Schlösing, A. Pagnoul, B. Tacke, H. Immendorff, V. Alpe and A. Menozzi, M. W. Beyerinck and A. van Delden, M. Gerlach and I. Vogel, E. von Freudenreich, A. Koch, S. Winogradsky, F. Löhnis and T. Westermann, etc. It has long been known that leguminous plants—peas, beans, clover, lupins, alfalfa, etc.—enrich the nitrogen content of soils. These plants have the remarkable power of producing comparatively large quantities of nitrogenous proteids even when nitrogen compounds are absent from the soil. Plants like the gramineæ can do this only when nitrogenous food is at their disposal in the soil itself. The fact was mentioned in 1808 by A. D. Thaer, and H. Davy said that the nitrogen contained in peas and beans is derived from the atmosphere. These observations were abundantly confirmed by J. B. J. D. Boussingault, G. Ville, J. B. Lawes and J. H. Gilbert, H. Hellriegel and H. Wilfarth, C. Schulze, M. H. Maercker, E. Gatellier, W. O. Atwater, J. Lutoslawsky, P. Wagner, and T. Schlösing and E. Laurent. Nodules on the roots of these plants were studied by M. Malpighi, J. Dalechamps, P. Boccone, A. P. de Candolle, L. C. Treviranus, H. Lachman, J. Erikson, A. Cornu, T. Dyer, E. Warming, L. Kny, A. B. Frank, E. E. Prillieux, etc. The nodules on the rootlets of a *phaseolus* are illustrated by Fig. 55. A magnified cross-section is shown in Fig. 56. They were considered to be a pathological condition, and G. Gasparrini, and M. Woronin observed that the parenchyma cells of the nodules contained bacteria in short rod-like forms. F. Schindler suggested that these bacteria—which M. W. Beyerinck called *bacterium radicicola ;* and A. B. Frank, *rhizobium leguminosarum*—live with the plant in a kind of partnership, or symbiosis—from σύν, with ; βίωσις, living. The bacteria live as guests in nodules in the roots of their host, and probably in the neighbouring soil. The symbiotic bacteria work up the nitrogen of the atmosphere in a form available as food for the plant on which they live. These bacteria are present in the soil, they penetrate the root hairs of legumes, grow into the cortex

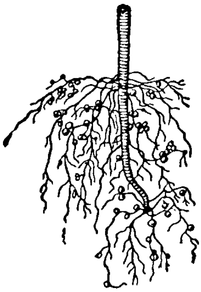

FIG. 55.—Tubercles or Nodules on Root of Bean Plant.

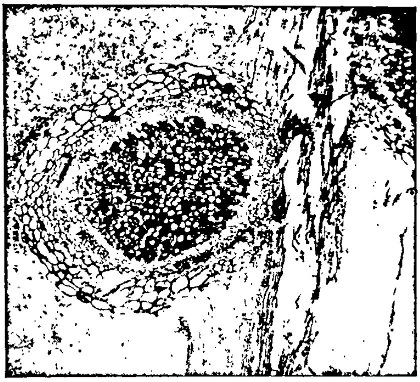

FIG. 56.—Cross-section through the Root-nodule of the Bean.

of the roots, and induce the formation of the tubercles. The bacteria multiply and pass into the tissue of the developing tubercle. These observations were established by the work of A. Prazmowsky, H. Hellriegel, R. Greig-Smith, G. E. Mattei, L. Montemartini, H. Möller, Z. Kamerling, B. L. Issatschenko, M. W. Beyerinck, A. Sperlich, A. Trotter, E. R. Spratt, L. Koch, G. Nicolas, E. Jülg, J. Brunchorst, O. Mattirolo and L. Buscalioni, A. Tschirch, A. B. Frank, E. Warming, P. Schürhoeff, P. E. L. van Tieghem and E. Douliot, G. F. L. Sarauff, W. B. Bottomley, O. Zinsser, J. Golding, J. Levy, E. Bréal, L. Albert, A. L. Whiting, J. Stoklasa, P. P. Dehérain and E. Demoussy, F. Noble and co-workers, etc. E. Kayser and H. Delaval observed that the presence of a radioactive uranium mineral increased the activity of nitrogen-fixing bacteria. A. W. Bosworth and co-workers observed that ammonia is produced by the human tubercle bacillus.

The chemical actions which occur in the fixation of nitrogen under these conditions have been studied by L. Hiltner, but the results are indefinite. Many soils are very deficient in the bacterium radicicola, and experiments have been made by numerous workers—A. P. Aitken, C. Barthel, G. Bredmann, H. R. Christensen, R. Combes, A. Eichinger, H. von Feilitzen and co-workers, A. B. Frank, E. B. Fred, W. Golte, E. Grabner, L. Hiltner, K. F. Kellerman and co-workers, T. Imasehki, G. Kock, A. Kühn, E. Laurent, C. P. Lipman and L. W. Fowler, F. Löhnis and S. Suzuki, M. H. Märcker and H. Steffeck, N. Makrinoff, O. Mattirolo and M. Soave, G. T. Moore, F. Noble and co-workers, V. Peglion, T. Remy, J. Schuloff, J. Simon, N. Strampelli, B. Tacke, A. Teichinger, E. Teisler, J. A. Völcker, etc.—with the object of impregnating soils with the bacteria so necessary for the full development of leguminous plants. A number of cultures of these bacteria have been placed on the market so that soils can be readily inoculated, For example, there are F. Noble and L. Hiltner's *nitragen ;* J. Simon's *azotogen ;* G. T. Moore's culture, *nitrobacterine ; bacterized peat ;* etc. In a way, the results have been fairly satisfactory for certain crops when peptones and glucose were added to the water in which the nitrifying bacteria are distributed for spreading on the soil.

The early workers—S. Hales, J. Ingenhousz, and J. Priestley, for example, *vide* **1.** 3, 7—on the assimilation of food by plants were more particularly concerned with the changes produced in the atmosphere surrounding the plant, and little progress could be made until the composition of air and water had been established. J. Priestley had the opinion that free nitrogen could be assimilated by the higher plants ; while N. T. de Saussure, on the contrary, thought that nitrogen was given off by them. He also concluded that plants derive their food from air and water—the nitrogen being derived from the ammonia and nitrogenous matters in the soil ; and the mineral constituents, also from the soil. The evidence adduced by J. B. J. D. Boussingault, J. B. Lawes and co-workers, was one time taken to prove that green plants, without the aid of bacteria, cannot fix elementary nitrogen from the atm. G. Ville, however, contended that some green plants do possess this power, and T. Jamieson, E. Mameli and G. Pollacci, B. Moore and co-workers, F. B. Wann, and C. B. Lipman and J. K. Taylor showed that wheat, barley, and some other plants can gain nitrogen at the expense of atm. air without the nitrogen being first fixed by bacteria, and then passed on to the plant ; peas cannot fix nitrogen without the aid of bacteria ; while the *Bromus villosus* can do so to a slight extent. It is assumed that the fixation of nitrogen occurs in the cells of the green leaves. The physiological action is discussed in works by A. Fischer, K. W. Jurisch, E. Abderhalden, H. Frölich, G. Stahel, C. Ternetz, P. Haupt, etc.

E. C. C. Baly and co-workers [2] showed that soln. of nitrates and carbonic acid are respectively converted into nitrite and formaldehyde in ultra-violet light, and these products then react to form formhydroxamic acid ; this acid then combines with more photosynthesized formaldehyde to give a variety of products —*e.g.* glyoxaline, free and substituted α-amino-acids, and substances of an alkaloidal nature. Methylamine and pyridine are produced by the action of photochemically activated formaldehyde on ammonia. According to O. Baudisch, cholera bacilli rapidly reduce nitrates to nitrites, and the velocity of the reaction is dependent on the bacterial iron content. Dextrose in alkaline soln. reduces nitrites, but not nitrates, and then only in the presence of traces of iron. Ferrous hydrocarbonate, or hydroxide, does not reduce alkali nitrates even at 100° in the absence of oxygen ; the presence of oxygen, however, causes immediate reduction to nitrite, and there is a direct relation between the amount of oxygen dissolved in the water and the amount of nitrite formed. This " fertilization " process involves the production of a peroxidic iron compound, nitrite, and the reactive intermediate substance potassium nitrosyl, KNO. The latter substance reacts with aldehydes with the formation of hydroaximic acids, OH.N : N.OH. The magnetic properties of the peroxide are directly related to its great chemical activity. The action of potassium pentacyanoperoxoferrate, $K_3[FeO_2(NC)_5]$, in behaving as an oxygen carrier and activator is likened to a simple type of respiration. Whilst light of long wave-length brings about the formation of an alkaline aquobase from potassium ferrocyanide soln., the reduction of alkali nitrates is effected only by light of short wave-length. In summer sunlight, alkali nitrates can be reduced to nitrite in a short time if small quantities of complex salts, *e.g.*, potassium ferrocyanide, are present. Formaldoxime and formaldehyde in sunlight form cyclic nitrogen compounds which contain pyridine and pyrrole rings and give the typical alkaloidal reactions. An aq. soln. of acetaldoxime and formaldehyde when exposed to sunlight gives a thick, dark brown syrup which has not been investigated. Nitromethane also unites with formaldehyde under the influence of light, or in weakly alkaline soln., isonitrobutylglycerol being formed intermediately. The illumination of alkali nitrates with daylight in the presence of formaldehyde yields gases agreeing qualitatively with those formed by soil bacteria, and (in the presence of iron salts) formhydroxamic acid and formaldoxime. It is possible that many soil bacteria and also green leaves utilize nitrous oxide from the air for nitrogen nutrition. Although at considerable altitudes, or by the influence of silent electric discharges, carbon dioxide can be reduced to formaldehyde, which may then react with nitrous oxide from atm. nitrogen and oxygen to yield formhydroxamic acid, it is thought possible that the reduction can be effected by sunlight at sea-level without the aid of chlorophyll. N. R. Dhar and R. P. Sanyal found that while ultra-violet light is more effective in certain photosyntheses, yet tropical sunlight contains a number of rays which can effect the synthesis of complex compounds from simple substances. Methylamine, which is formed in about 12 hrs. when ammonia and formaldehyde are exposed to tropical sunlight, passes into a number of complex substances of the alkaloid type. In violet-light, nitrogen and oxygen combine to form nitrogen oxides. The difference between the action of sunlight and ultraviolet light in promoting photosynthesis is one of degree rather than of kind.

The nitrogen cycle.—All living matter, and the waste products of animals contain considerable quantities of combined nitrogen. This element is a necessary constituent for the growth of living organisms. During the decay of organic matter through the agency of bacteria, part of the nitrogen finds its way back to the atmosphere, and part passes directly into the soil to be absorbed by plants. Animals cannot assimilate free nitrogen, and they are accordingly dependent upon the plants for their supply ; nor can the plants usually obtain the nitrogen they require direct from the atmosphere. Most plants get their nitrogen from the soil where it is present in the form of nitrates, ammonium, or other complex compounds. The organic matter in the soil is attacked by bacteria of various kinds, and part is converted into nitrates and part into free nitrogen. A certain amount is brought back from the atmosphere, during rain storms, where it has been oxidized into ammonium nitrate by electric discharges. These supplies of available nitrogen, however, do not suffice to maintain the fertility of cultivated soils. It is therefore necessary to make good the constant draining of the available nitrogen by the cultivated plants. This is done by allowing nitrogenous matter —manures—to decay in the soil, or to add to the soil a mixture—fertilizer—containing available nitrogen and other plant foods. The processes involved in the circulation of nitrogen in nature may be summarized in the scheme :

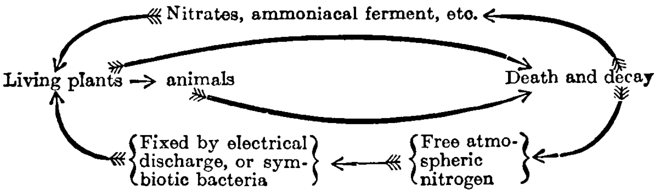

FIG. 57.—The Nitrogen Cycle.

The idea has been expressed in a more romantic way. To-day a nitrogen atom may be throbbing in the cells of the meadow grass ; to-morrow it may be pulsating through the tissues of a living animal. The nitrogen atom afterwards may rise from decaying animal refuse, and stream to the upper regions of the atmosphere, where it may be yoked with oxygen in a flash of lightning and return as plant food to the soil in a torrent of rain ; or it may be directly absorbed from the atmosphere by the soil, and there rendered available for plant food by the action of symbiotic bacteria. Thus each nitrogen atom has doubtless undergone a never-ceasing cycle of changes through countless æons of time.[3]

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§ 31. The Fixation of Atmospheric Nitrogen by Direct Oxidation

The consumption of nitrogenous matters in the cultivation of lands cannot be made good by the nitrogen compounds formed by natural processes. Nature's way of restoring nitrogen to soils is by bacterial action, and electrical discharge in the atmosphere, which cause the union of oxygen and nitrogen, and, according to J. von Liebig,[1] this results in the production of about 10·3 to 16·2 lbs. of combined nitrogen per acre per annum. B. Moore also has shown that it is possible that some fixation occurs by the action of solar rays. The development of agriculture is largely dependent on the cheap production of nitrogen in a form available for plant food. The cultivation of wheat, for example, is largely dependent upon nitrogenous manures. Not many years ago, the supplies of available nitrogen were derived from the Chilean and other natural deposits of nitrates; and the ammoniacal salts obtained as a by-product in the manufacture of coal-gas, and coke. The production of nitrates by bacterial action, and in nitre-plantations—2. 20, 36—is utterly inadequate to supply the growing needs of agriculture when supplemented by animal excrementa and refuse, and sewage sludge. Although the nitre beds of Chile and Peru contain millions of tons of nitre, yet the outlook was not hopeful because it was estimated that the beds would be approaching exhaustion in about a century. Most of the nitre is used as a fertilizer for wheat, etc. Wheat is the staple food of the white races. Consequently, W. Crookes could say in 1898, " The fixation of nitrogen is vital to the progress of civilized humanity, and unless we can class it among the certainties to come, the great Caucasian race will cease to be foremost in the world, and will be squeezed out of existence by races to whom wheaten bread is not the staff of life." The problem has since been solved. The atmosphere contains about 4×10^{15} tons of nitrogen, so that there are about 20 million tons of nitrogen over each square mile of the earth's surface; this is over 30 times that produced per annum as Chile saltpetre and by-product ammonia. There is therefore present at hand an enormous supply from which the nitrogen can be borrowed for the preparation of plant food. The supply is inexhaustible because, in due course, it is returned to the atmosphere as elemental nitrogen by the operation of nature's perpetual cycle.

Just as during the Napoleonic wars, when the French ports were closed, the need for nitrates for the manufacture of gunpowder stimulated the beleaguered French to cultivate nitre-plantations (2. 20, 36), so also during the 1914–18 war, the need for nitrates for the manufacture of explosives stimulated the beleaguered Germans to develop methods for the fixation of atm. nitrogen in the form of nitrates. As a result, in 1917, they were making nitric acid from atm. nitrogen at the rate of 320,000 tons per annum, whereas in 1914, only one-fifth of this amount was produced. Otherwise expressed, the nitrogen fixation processes contributed only 4·5 per cent. of the world's consumption of nitrates and ammonia in 1912; this had increased to 43 per cent. in 1920; and now, fixation processes furnish the largest proportion of the world's requirements.

Several solutions of the problem so clearly stated by W. Crookes have been devised, some of these processes are now competing industrially, others are a little more costly, and are in consequence not in operation. The more important ways of fixing atm. nitrogen are: (i) The direct oxidation of nitrogen to its oxides so as to furnish nitric acid or nitrates, as typified in the arc processes; (ii) The direct combination of nitrogen with hydrogen to form ammonia as typified by F. Haber's process—*vide supra;* (iii) The absorption of nitrogen by the metals which subsequently form ammonia when treated with water as typified by O. Serpek's process —*vide supra;* (iv) The absorption of nitrogen by carbides as exemplified by the cyanamide process of A. Frank and N. Caro. More nitrogen is fixed by this process than by any other one. (v) The conversion of atm. nitrogen into cyanides as exemplified by J. E. Bucher's process; and (vi) The oxidation of nitrogen during the combustion of coal gas or natural gas as proposed in F. Häusser's, and O. Bender's processes.

About 1775, J. Priestley[2] passed a series of electric sparks through atm. air confined in a suitable vessel over water coloured purple by a decoction of turnsole or archil. He found:

> The most important though least expected observation was that the upper part of the liquor became red, and in proportion as the red extended so did the liquid rise in the vessel, diminishing the space in which the sparks were passing. He found that the air contracted one-fifth of the whole space, after which more sparking produced no sensible effect.

It was at first thought that fixed air—carbon dioxide—was produced, but when H. Cavendish repeated the experiment, the absence of any signs of turbidity was taken to prove that carbon dioxide was not produced by the electrification of atm. air. H. Cavendish then proved that the product of the action is nitrous or nitric acid. In his experiments on the production of water by the explosion of mixtures of inflammable air (hydrogen) and common air, H. Cavendish found that if a mixture of oxygen and hydrogen is exploded the dew which results is not pure water, but water containing nitric acid, which when neutralized with alkali and evaporated, furnished crystals of nitre. This result was embarrassing, for if water and water only is derived from the explosion of hydrogen and common air, in which the contained oxygen is alone consumed, why is water not derived, *à fortiori*, when the nitrogen of the atm. is excluded, and when the elements oxygen and hydrogen are exploded in their just proportions with each other? Whence comes the nitric acid? In January, 1783, H. Cavendish proved that the nitric acid is derived from the nitrogen of the atmosphere, and that if the hydrogen and oxygen be properly purified, no acid is formed. By gradually increasing the proportion of nitrogen added to a mixture of hydrogen and oxygen, the quantity of nitric acid is increased, but there is a limiting value, since when the proportion of nitrogen approaches that of air, the heat produced by the explosion is so much diminished as to be incapable of determining the formation of nitric acid, and water alone is formed. H. Cavendish also showed that by passing an electric spark repeatedly through a mixture of atm. air and oxygen, confined in a bent glass tube by columns of mercury and soap-lees, nitric acid is formed, which, uniting with the alkali of the soap-lees, forms nitre. The process is slow and tedious, and failed in the hands of M. van Marum and P. van Trootswyk in Holland, and of A. L. Lavoisier, and G. Monge in France. In consequence, it was repeated three times under H. Cavendish's own directions before a committee of the Royal Society, and the result fully established.

The fixation of nitrogen by electrical discharges.—H. Davy[3] studied the formation of nitric acid during the electrolysis of water in the presence of air— **1.** 3, 6—and C. F. Schönbein explained this on the assumption that ozone is first formed, and that this attacks the nitrogen, forming nitrogen peroxide; but

L. Carius showed that ozone does not attack nitrogen either at ordinary or at elevated temp. R. Böttger, A. Perrot, and H. Buff and A. W. Hofman found that induction sparks quickly form nitrous fumes in dry or moist atm. air. G. Meissner said that only ozone is formed by the spark or silent discharge in dry air, but in moist air, nitrogen peroxide is formed. He said that ozonized air passed through water produces nitric acid, but this statement awaits verification. The formation of nitric acid by the action of the silent discharge on air passing through an ozonizer was noted by J. B. Lawes and co-workers, P. Hautefeuille and J. Chappius, C. F. Harding and K. B. McEachron, H. Spiel, E. W. von Siemens and J. G. Halske, W. Löb, M. Berthelot, S. Cloez, S. de Luca, R. Sellentin, and J. von Kowalsky. A. Findlay likewise observed the formation of nitric acid and during the action of Tesla's brush discharge on a mixture of moist oxygen and nitrogen. A. Makowetzky used an apparatus consisting of an H-tube containing dil. sulphuric acid. One limb contained the platinum electrode, through which the current passed into the acid ; the gas evolved at it was collected separately. Above the surface of the acid in the other limb, which was closed so that the gaseous products could be collected, the second electrode was placed. The arc was formed between this second electrode and the surface of the dil. acid. The second electrode was sometimes a water-cooled platinum tube, sometimes a Nernst glower, which was allowed to become hot. When the arc is formed in an atm. of nitrogen using the liquid surface as anode and a hot cathode, the only products are hydrogen and a little ammonia. When the current is reversed, oxygen, hydrogen, hydrogen dioxide, ammonia, and nitric acid are formed. The hydrogen dioxide is formed at the surface of the liquid owing to the very large cathode fall of potential. The gas at the surface of the liquid is almost entirely steam, which is probably decomposed into hydrogen dioxide and hydrogen ; as much as 9 millimols of the former per 1000 coulombs were found. The yields of ammonia and nitric acid are greatest with about 0·04 ampere (about 2 millimols per 1000 coulombs), and they appear to be formed throughout the length of the arc. K. B. McEachron[4] studied the form of the containing vessel on the production of nitric oxide by the high-voltage electric discharge. G. M. Schwab and S. Loeb obtained nitric oxide by the action of a cold, direct current discharge with an oxide cathode on a mixture of nitrogen and oxygen at 6 mm. press. It is assumed that the greater part of the energy taken from the oxygen serves to activate the nitrogen by impact of the oxygen ions on the nitrogen mols., whilst the energy absorbed by the latter for which the absorption law applies is, under the experimental conditions, only a small part of the current energy, which is mainly lost by reflection from the electrodes.

The first serious attempt to utilize H. Cavendish's reaction for burning atm. nitrogen was made in 1859 by L. J. P. B. Lefebure. She obtained a patent for making nitric acid by passing sparks through air, and absorbing the product in alkali-lye ; but the process did not come to anything. In 1880, W. Spottiswoode and J. F. Moulton observed that a flame is excited by means of an alternating current, and W. Crookes, in 1892, showed that the effect is due to the burning of the nitrogen. He said :

> Nitrogen is a combustible gas ; that is to say, a mixture of nitrogen and oxygen (atmospheric air) will under certain conditions burn with a flame, and production of nitrous and nitric acids. The reason why, when once nitrogen is set on fire, the flame does not spread throughout the whole atmosphere and deluge the world in a sea of nitric acid, is that the igniting-point of nitrogen is higher than the temperature produced by its combustion, and therefore the flame is not hot enough to set fire to the adjacent gas. The temp, is a little higher than that of a good blow-pipe flame, easily melting fine platinum wire. The hot gases rising from a flame have a strong odour of nitrous acid, and when it is produced in a closed globe, the interior rapidly fills with red gases.

In 1897, Lord Rayleigh isolated argon from atm. air by confining a mixture of 9 vols. of air and 11 vols. of oxygen in a glass globe in which the electric flame was developed—*vide* argon. He obtained a yield eq. to 49 grms. of nitric acid per kilowatt hour. By using an alternating current of 60 periods per second and 8000 volts, A. McDougall and F. H. Howles obtained a yield of 65 grms. of nitric acid per kilowatt hour. J. de Kowalsky increased the yield still further by using a current of 0·05 amp., 50,000 volts, and 6000–10,000 periods per sec.; while C. S. Bradley and D. R. Lovejoy obtained a yield of 88 grms. of nitric acid per kilowatt hour by substituting arcs quickly torn away from the electrodes so as to furnish a series of isolated sparks or arcs.

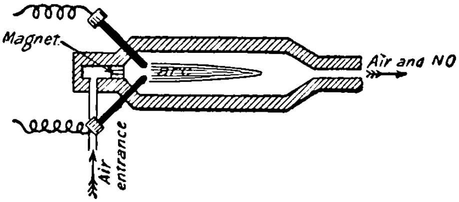

FIG. 58.—E. W. von Siemens and J. G. Halske's Experiment.

In E. W. von Siemens and J. G. Halske's experiment, Fig. 58, nitrogen was burnt by passing air through a powerful electric arc spread over as great a surface as possible by means of an electromagnet. In 1903, K. Birkeland and S. Eyde established a factory, the Norsk Hydroelektrisk Kuaelstofaktieselskab, at Notodden, Norway, for the fixation of atm. nitrogen as nitrites and nitrates. It was found that with the ordinary arc-flame, the hot space is relatively small and the conditions for rapid cooling are bad; with intermittent sparking or arcing, the conditions for rapid cooling are better. The arc is spread out or dispersed by a magnetic field, and accordingly, the air in the arc itself is very hot; but just outside the arc, the air is comparatively cool, so that the nitrogen oxides formed in the arc are cooled, at once, just outside the arc. Hence, when air is heated in the electric arc in order to oxidize the nitrogen, short thick arc flames are to be avoided. In 1905, A. A. Naville and P. A. and C. E. Guye showed that if the nitrous oxide be allowed to accumulate, the rate of oxidation per unit of energy employed is greatly diminished; and in consequence, (1) the oxidized air should be removed as speedily as possible from the sparking chamber, and (2) the sparking chamber should be as small as possible to hinder the diffusion of oxidized air into the fresh air entering. J. Brode, F. O. Anderegg and co-workers, K. B. McEachron and co-workers, and A. Geitz studied the oxidation of nitrogen in the high-tension arc flame.

M. Berthelot found that when a mixture of nitrogen and an excess of oxygen is sparked over alkali-lye, an excess of nitrite over nitrate is always produced. This would not be the case if the nitrogen was oxidized to nitrogen peroxide. He accordingly supposed that the two gases first combine to nitric oxide, and that this is then oxidized to nitrous anhydride, which in turn is partly oxidized to nitric peroxide, and part is absorbed as such. Nitrogen is so stable at ordinary temp. that instead of exhibiting a tendency to oxidize, the oxides tend to break down into their elements. The first step in the oxidation is to convert the nitrogen to nitric oxide. The nitric oxide is subsequently converted by the atm. oxygen into nitrogen peroxide. W. Muthmann and H. Hofer first attempted to measure the equilibrium conditions of the reversible reaction $N_2+O_2\rightleftharpoons 2NO$, at different temp., employing a high-tension alternating current arc between platinum electrodes. The measurements were subsequently extended by W. Nernst and his co-workers, K. Finckh, and K. Jellinek, by F. Haber and co-workers, and others. The equilibrium constant, K, for the reaction: $N_2+O_2\rightleftharpoons 2NO$, is $[O_2][N_2]K=[NO]^2$. It is of course probable that if the temp. were to be raised high enough, the mols. of nitrogen and oxygen would be dissociated into atoms; the endothermal reaction $N_2+O_2=2NO$ would become exothermal $N+O=NO$; and the conc. of the nitric oxide thereafter diminish with rise of temp. If x denote the percentage of nitric oxide by vol. at equilibrium, starting with air containing 79·2 per cent. of nitrogen and 20·8 per cent. of oxygen, $x^2=K(79{\cdot}2-\tfrac{1}{2}x)$. Then, W. Nernst and fellow-workers showed that with air,

0° .	1538°	1604°	1760°	1922°	2307°	2402°	2627°	2927°
x Obs.	0·37	0·42	0·64	0·97	2·05	2·23	—	—
x Calc.	0·35	0·43	0·67	0·98	2·02	2·35	3·18	4·39

where the calculated values are derived from the equation $\log_{10}(K/K_1) = Q/2{\cdot}3R\{(T_1-T)/TT_1\}$, when the conc. of nitric oxide from air at 2200° K. is 0·99 per cent. The formation of nitric acid is an endothermal process, and these results are in agreement with the general law that a rise of temp. displaces the equilibrium in a direction which favours the formation of an endothermal compound. The observed values of K at atm. press. are :

°K. .	1811°	1877°	2023°	2033°	2195°	2580°	2675°
log K Obs.	−4·08	−3·97	−3·59	−3·60	−3·23	−2·57	−2·49
log K Calc.	−4·13	−3·95	−3·59	−3·57	−3·23	−2·58	−2·45

where the observed values are calculated from I. W. Cederberg's expression $\log K = -9444T^{-1}+0{\cdot}000372T^{10{\cdot}75}+0{\cdot}399$. W. Nernst gave $\log K=1{\cdot}63-9450T^{-1}$; and also $\log K=1{\cdot}09-9452T^{-1}$; J. Boner, $\log K=1{\cdot}60-9450T^{-1}$; W. G. Shilling gave $\log K=-9397T^{-1}-1{\cdot}75 \log T+0{\cdot}00680T-0{\cdot}0_5297T^2+0{\cdot}0_9442T^3+1{\cdot}6$. C. P. Steinmetz, $\log_{10} K=1{\cdot}048-9380T^{-1}$. In the case where a mixture of equal vols. of nitrogen and oxygen is used, $K(50-\frac{1}{2}x)^2=x^2$, or, since x is small, $x=50\sqrt{K}/(1+\frac{1}{2}\sqrt{K})$, very nearly, and with air, $x=40{\cdot}8\sqrt{K}/(1+0{\cdot}52\sqrt{K})$, very nearly. This makes the yield with a mixture of equal vols. of nitrogen and oxygen about 18 per cent. greater than is the case with air. The gases leaving the combustion chamber must be cooled to ordinary temp. before they can be analyzed. Hence, if the cooling takes place slowly, the high temp. equilibrium will be displaced, forming a new state corresponding with the temp. at which the velocity of the reaction is negligibly small. Hence, it is imperative to cool the gases so rapidly that there is no time for a change from the high temp. equilibrium to that of a new state. H. V. Tartar and M. F. Perkins found that with a high tension arc, and a gas velocity through the arc of 330 litres per hour, the equilibrium, approached from both sides, at atm. press., is that shown in Fig. 59. M. le Blanc and W. Nüranen found that below 300°, the reaction is bimolecular, and above that temp., a unimolecular reaction sets in. In the former case, k_1 denotes the velocity constant for the formation of nitric oxide, and k_2, that for the decomposition of nitric oxide. If the rate of formation of nitric oxide be dx/dt, then, if C_1 and C_2 respectively denote the vol. percentages of nitrogen and oxygen gases, and x, that of nitric oxide, $dx/dt=K_1(C_1-\frac{1}{2}x)(C_2-\frac{1}{2}x)-k_2x^2$. C. P. Steinmetz gave $\log_{10} K_1 =0{\cdot}161+5{\cdot}731\times10^{-3}T-9380T^{-1}$; and $\log_{10} k_2=9{\cdot}113 +5{\cdot}731\times10^{-3}T$. K. Jellinek has measured the velocity constants, k_1 and k_2, and found them to be much affected by variations of temp. The time required for half the decomposition of nitric oxide into nitrogen and oxygen approximates to $t_2=1/k_2$; and the time needed for half the theoretical production of nitric oxide is $t_1=1{\cdot}36k_1^{-\frac{1}{2}}k_2^{-\frac{1}{2}}$. K. Jellinek found, for atm. press.,

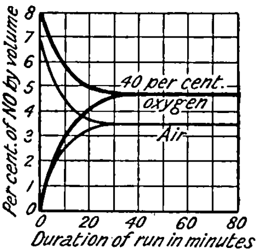

FIG. 59.—Equilibrium in the Oxidation of Nitrogen with Air, and Oxygen-enriched Air.

°K..	1000°	1500°	1900°	2100°	2500°	2900°
k_1 .	$4{\cdot}0\times10$	$3{\cdot}78\times10^4$	$9{\cdot}06\times10^6$	$1{\cdot}40\times10^8$	$3{\cdot}37\times10^{10}$	$8{\cdot}07\times10^{12}$
k_2 .	$1{\cdot}74\times10^{-7}$	$2{\cdot}33\times10^{-1}$	$1{\cdot}20\times10^3$	$5{\cdot}55\times10^4$	$6{\cdot}98\times10^7$	$5{\cdot}48\times10^{10}$
Time	81·62 yrs.	1·26 days	2·08 min.	5·06 sec.	$1{\cdot}06\times10^{-2}$ sec.	$3{\cdot}45\times10^{5}$ sec.

Here, at the absolute temp. indicated, the period of time is that required for the formation of half the possible conc. from air. On the other hand, the periods of time required for the complete decomposition of half a given quantity of nitric oxide at atm. press. are $7{\cdot}35\times10^3$ min. at 900° K.; $5{\cdot}80\times10^2$ min. at 1100° K.; 44·3 min. at 1300° K.; 3·3 min. at 1500° K. and $1{\cdot}21\times10^{-3}$ min. 2100° K. E. Briner and co-workers represented their results by $\log (C^2_{\mathrm{NO}}/C_{\mathrm{N_2}}C_{\mathrm{O_2}})=1\cdot63-9452T^{-1}$; and S. W. Saunders obtained fairly good results with $\log K_p=1\cdot0-9452T^{-1}$. C. P. Steinmetz has made more elaborate calculations. The results show that the state of equilibrium, $N_2+O_2\rightleftharpoons 2NO$, is attained at very high temp. in a very short time; and that below 1000°, the rate of decomposition of nitric oxide is so slow as to be negligible for industrial purposes. Hence, assuming that the reaction is purely thermal, the best results with air should be obtained by working above 3000°, and cooling below about 1000° with the utmost celerity. The most convenient way of obtaining the required high temp. is the electric arc, and no other method has been successful. J. Boner studied the results obtained in the oxidation of nitrogen to nitric oxide with platinum as a catalytic agent, and also when the platinum is associated with the alkaline earths as promotors.

The only conclusion W. Muthmann and H. Hofer, H. V. Tartar and M. F. Perkins, and W. Nernst could draw from the close agreement between the observed and calculated values of x, was that the reaction is purely thermal in that the reaction observed is solely produced by the absorption of heat; and there is no deviation from the law of mass action due to special electrical effects; and H. V. Tartar and M. F. Perkins obtained no evidence that a reduction of press. would increase the efficiency of the process. M. le Blanc and W. Nüranen found that the equilibrium constant, K_1, was not affected by changes in the conc. of the initial mixture ranging from 3·2 to 87·1 per cent. of oxygen. A. Grau and F. Russ observed that the value of K increased with increasing proportions of oxygen, and attributed this to the increased temp. of the arc, because the electrical energy in watts required to maintain the arc simultaneously increased. They assumed, therefore, that an equality of watt-consumption was an approximate criterion of the equality of the temp. of the arc; and they found that the values of K were in harmony with the assumption that the process is purely a thermal one. They also found that the equilibrium in the high-tension arc is not influenced when the press. changes from 761 to 847 mm. in harmony with the law of mass action for reactions in which the number of mols. does not change. F. Förster, and H. Lee and A. Beyer found the yields were practically identical with the direct and alternating current discharges, and hence concluded that reaction in the arc is not affected by electrical influences, but is purely a thermal process. F. Haber and co-workers obtained much larger yields of nitric oxide than were obtained by W. Nernst, and by extrapolation, the results would represent impossibly high temp.—say, 5000° K. Thus, while W. Nernst obtained 5 per cent. of nitric oxide at 3200°, F. Haber and A. König found that the percentage amount of nitric oxide formed increases with current up to a maximum, and then is not affected by a further increase of current. They worked with press., ranging from 40 to 200 mm. The greatest yield of nitric oxide was obtained at 100 mm. press.

Oxygen initially present .	20·9	48·9	44·4	75·0	81·7 per cent.
Nitric oxide produced .	9·8	14·4	14·3	12·77	12·1 „ „

Hence, some influence must be at work other than the purely thermal change represented by the equilibrium $N_2+O_2\rightleftharpoons 2NO$. E. Briner and E. L. Durand, and P. A. Guye consider that our knowledge of the high temp. equilibrium of nitric oxide is based on values extrapolated from observation at much lower temp. and that subsidiary reactions such as dissociation of nitrogen and oxygen to atoms or ions would explain the production of greater proportions of nitric oxide than are predicted by the extrapolation.

M. Berthelot, in 1877, stated that nitrogen and oxygen do not form nitrogen oxides under the influence of the silent discharge, but in 1906, he showed that the gases do unite under this condition. H. Fischer observed that with a Tesla current of 10,000 volts, a mixture of nitrogen and oxygen furnishes small quantities of nitrogen pentoxide, no nitric oxide, and a yield of ozone which increases with increasing conc. of oxygen. A. Gunther-Schulze observed that nitrogen and oxygen react only slightly in the glow discharge, and C. Boissonnas studied this reaction. D. Berthelot and H. Gaudechon observed no reaction in the light of a quartz mercury lamp. E. Warburg and G. Leithäuser definitely proved that nitric oxide is produced by the silent electrical discharge in air at ordinary temp. when the thermal equilibrium virtually corresponds with no formation of nitric oxide. Hence, said E. Warburg, the formation of nitric oxide in the arc cannot be a purely thermal process, but electrical influences—say electronic collisions—must play a part, F. Haber and co-workers argued that the primary action in both the high-tension arc and in the silent discharge is electrical. F. Haber and A. König said that the kinetic energy of the gaseous ions and of the electrons produced in the arc, moving under the potential gradient between the electrodes, is directly utilized in forming nitric oxide by collisions of the ions and electrons and with one another and with the neutral molecules. The greater the difference of potential between the electrodes, the greater will be the kinetic energy of these ions and electrons, and the greater the production of nitric oxide. In time, a state of electrical equilibrium will be attained in which an equal number of mols. of nitric oxide is formed and decomposed by the electronic and ionic impacts. While the thermal equilibrium is determined only by the mass law and temp., the electrical equilibrium is also affected by the amount of electrical energy expended per unit time, and this also determines the difference between thermal and electrical equilibria. The difference is shown by the fact that the equilibria conditions in the action of the silent discharge in the reactions : $3O_2 \rightleftharpoons 2O_3$; $2CO + O_2 \rightleftharpoons 2CO_2$; and $N_2 + 3H_2 \rightleftharpoons 2NH_3$, at ordinary temp. are the same as the thermal equilibria at higher temp. The slowness of the reverse change at ordinary temp. accounts for the fact that the electrical equilibria are preserved when the electrical stimulus is withdrawn. If the temp. is so high that the thermal equilibrium is attained very rapidly, the electrical equilibrium will be subordinated to the thermal equilibrium, and the observed conc. of nitric oxide will correspond to the purely thermal condition any excess due to the electrical stimulus will be at once decomposed, when the electrical stimulus is withdrawn. Hence, the electrical equilibrium will be dominant only when the temp. is low enough to decompose the nitric oxide very slowly. F. Haber was able to realize this condition experimentally, by passing the gases slowly under diminished press. through narrow tubes completely filled by the arc, and cooled by a water-jacket. The yields of nitric oxide were much higher than corresponded with the simple thermal equilibrium at the temp. of the arc. Hence it was argued that the use of a low temp. arc gives better results than a high temp. arc, although the cold arc has not yet been worked industrially. The reason W. Nernst and fellow-workers obtained results in agreement with purely thermal equilibria, when working with the high tension arc, is due to the rapid secondary thermal decomposition of the nitric oxide. The thermal influence got the upper hand of the electrical. F. Haber and A. König hold that in the work of W. Muthmann and H. Hofer, A. McDougall and F. H. Howles, and J. Brode, the assumed temp. were not attained, and that in these short high-tension arcs, with alternating currents, the temp. must vary enormously at every part of the arc so that it is almost meaningless to speak of an average temp., and apply the result to calculate thermodynamic equilibrium. The high results, 6·7–7·4 per cent. of nitric oxide, obtained under these conditions might well be attained at the possible temp. of 3500°, but the thermal equilibrium at such a temp. would be so mobile that it is very improbable the conc. of nitric oxide actually attained could be maintained by rapid cooling. Hence, it is more probable that the observed results represent a kind of electrical equilibrium. These conclusions were confirmed by the work of W. Holwech, W. Holwech and A. König, S. Karrer, G. W. Morden, and F. Haber, A. König, and E. Platou. G. M. Schwab and S. Loeb worked with a cold direct current discharge with an oxide cathode, and found the velocity of formation of nitric oxide with mixtures containing 20–80 per cent. of oxygen.

F. Fischer and E. Hene suggested that the apparent deviations from the mass law observed by A. Grau and F. Russ, and the high conc. of nitric oxide obtained by F. Haber and A. König with the cooled arc, are due to the activation of oxygen in the electric arc. It is assumed that the conditions in the electric arc are favourable to the formation of ozone, and that the nitrogen is oxidized by ozone. At first, with R. Escales, they thought in harmony with R. J. Strutt's observations, that the nitrogen was also activated, but since active nitrogen yields no nitric oxide in contact with oxygen, it was concluded that the nitrogen was not activated. They found that if ordinary nitrogen is allowed to mix with oxygen which has just been exposed to the spark discharge 6·5 times as much nitric oxide is formed as when ordinary oxygen is allowed to mix with the sparked nitrogen. In answer to A. König's question how any nitric oxide is produced at all if no activation of nitrogen occurs when sparked nitrogen is mixed with oxygen, they explained that the glowing nitrogen must have produced ozone when in contact with the oxygen. If a high-tension arc discharge be employed more nitric oxide is formed when air from the arc streams into oxygen than when it streams into air or nitrogen. F. Fischer and E. Hene did not think that the result can be explained by assuming that the mixing gas diffused into the arc flame because the watt-consumption in the arc remained constant in agreement with A. Grau and F. Russ' experiments. V. Ehrlich and F. Russ found that both nitric oxide and ozone are produced by the silent discharge in air at ordinary temp. The velocity of the reaction between ozone and nitrogen at ordinary temp. is too slow to test experimentally, but F. Fischer and E. Hene argued that if the formation of nitric oxide is due to the primary formation of ozone, the reaction should become perceptible at elevated temp. They found:

	20°	380°	430°	510°	700°
Nitric oxide . .	0·00	0·02	0·02	0·04	0·06 per cent.

No ozone was observed except at 20°; and no nitric oxide was formed at 700° without the discharge. They pointed out that the reaction $2O_3+N_2=2NO+2O_2+250$ Cals. is exothermal. It was therefore assumed that in the high-tension arc the oxygen is dissociated to atoms, and outside the arc, the atoms unite with oxygen mols. to form ozone. The formation of nitric oxide is assumed to be preceded by the activation of the oxygen, but whether oxygen atoms act directly on the nitrogen is not known. It is further suggested that the yields of nitric oxide might be improved by passing oxygen instead of air through the arc, and then mixing it rapidly with nitrogen. A. König objected to F. Fischer and E. Hene's conclusion that the nitrogen is not also activated, and believed that both gases are simultaneously activated. T. M. Lowry found that when air is passed through an ozonizer, or through a spark discharge, no nitrogen peroxide can be detected spectroscopically by a process sensitive to $\frac{1}{8000}$th part by vol.; but if the air be first passed through the ozonizer and then through the spark discharge, or *vice versa*, nitrogen peroxide is formed. O. Cramp and B. Hoyle also found that the yield of nitric oxide from the high-tension arc can be augmented by first ozonizing the air. T. M. Lowry also found nitrogen peroxide is formed by passing two currents of air through an ozonizer and spark discharge in parallel, and mixing the two currents. It was therefore assumed that the spark discharge produces a form of nitrogen which can be readily oxidized by ozone, but not by oxygen. The most advantageous method of oxidation is to produce the activated nitrogen in an atm. already charged with ozone; a less efficient method is to pass the air containing activated nitrogen into the ozonizer; and a still less efficient method is to mix air with activated nitrogen with ozonized air in a vessel a few feet away from the discharge apparatus. All this illustrates the instability of the activated nitrogen; a few seconds of time suffice for its reversion to a form oxidizable neither by oxygen nor by ozone. R. J. Strutt's active nitrogen did not give nitric oxide with ozone. The work of T. M. Lowry thus supports F. Haber and A. König's view that both oxygen and nitrogen are activated in the high-tension arc.

Assuming the temp. of the arc to be 2500°, F. Haber calculated the minimum expenditure of energy necessary to produce the corresponding amount of nitric oxide by the assumption that the reaction is purely thermal. This energy is the electrical equivalent of the heat absorbed in the reaction $N_2+O_2=2NO$, plus the heat required to raise the temp. of the gases to the temp. of the reaction. The mean sp. ht. of the three gases concerned in the reaction is taken to be $6{\cdot}8+0{\cdot}0006\theta$ cals. per mol, hence, $\frac{1}{2}(6{\cdot}8+0{\cdot}0006\times2500)=20{,}600$ cals. are needed per mol of nitric oxide; assuming the heat of formation of a mol of nitric oxide at 2500° is 21,600 cals.; therefore 42,200 cals. are needed for the production of 30 grms. or one mol of nitric oxide. This is eq. to nearly 0·05 kilowatt-hours per mol. In practice, one k.w.h. or one kilowatt-hour, with a 2 per cent. conversion, is needed for 30 grms. of nitric oxide. Hence, the energy efficiency of the arc process is about 5 per cent. Part of this can be utilized for heating boilers, etc. Hence, the arc process is very wasteful of energy, and can be employed economically only where cheap electrical power is available. This is possible in some of the hydroelectric plants in Norway, Switzerland, Canada, United States, etc. Since a mol of nitric oxide, by a series of spontaneous reactions, ultimately furnishes 63 grms. of nitric acid, the efficiency of the process is often expressed in terms of the quantity of nitric acid obtained from the nitric oxide per unit of energy—say in grams per kilowatt-hour, or in kilograms per kilowatt year. The high-tension arc, burning in air across horizontal electrodes, furnishes a true flame, the air-flame. This flame was studied by A. McDougall and F. H. Howles, W. Muthmann and H. Hofer, G. Brion, J. Brode, etc. The flame has three zones: (i) a luminous bluish band of light joining the electrodes. Here the current is carried across the air-gap, and, being heated directly by the current, the temp. is higher than in the other zones. Judging from the conc. of the nitric oxide in this zone, which J. Brode found to be about 8 per cent., the temp. is in the vicinity of 3700°. Surmounting the ozone is (ii) a broader bluish-green zone, and above this again is (iii) a feebly luminous brownish zone. The nitric oxide formed in the first zone here undergoes partial dissociation because higher conc. of this gas are obtained if this zone be cooled rapidly; some ozone is also decomposed in this zone. If the arc is formed in nitrogen gas, a single blue band is formed corresponding with the first zone of the air-flame; while the flame in oxygen gives zones corresponding with the first and second zones of the air-flame. Ozone was detected in this zone. Hence, the second zone in the oxygen- and air-flames, under conditions where it is absent in the nitrogen- or hydrogen-flame, is taken to prove that this is a zone of decomposing ozone. H. B. Moses obtained a sudden chilling of the gases and a correspondingly high yield by forming the arc over liquid nitrogen.

When the temp. of nitric oxide falls below 620°, it begins to oxidize, forming nitrogen peroxide: $2NO+O_2\rightleftharpoons2NO_2$, and below 140°, the reaction is complete—*vide* the dissociation of nitrogen peroxide, and nitric oxide. The nitrogen peroxide is absorbed by water giving a mixture of nitrous and nitric acids: $2NO_2+H_2O=HNO_3+HNO_2$; the nitrous acid is unstable under ordinary conditions, and decomposes: $3HNO_2=HNO_3+H_2O+2NO$; the nitric oxide is oxidized, forming more nitrogen peroxide, and thus the reaction goes on until all is converted into nitric acid: $4NO_2+O_2+2H_2O=4HNO_3$, in the presence of an excess of water. The nitric acid which results is therefore in dil. soln.—*vide* action of water and alkali-lye on nitrogen peroxide. With soln. of alkali hydroxide, at ordinary temp. and press., nitrogen peroxide forms a mixture of alkali nitrite and nitrate: $2NaOH+2NO_2=NaNO_3+NaNO_2+H_2O$. A mixture of equimolar proportions of nitric oxide and nitrogen peroxide behaves towards a soln. of alkali-lye as if it were nitrous anhydride, and produces alkali nitrite alone: $NO_2+NO+2NaOH=H_2O+2NaNO_2$. Hence, by choosing the right temp. for $2NO+O_2\rightleftharpoons2NO_2$, it is possible to prepare alkali nitrite (*q.v.*) alone from the oxidation products of nitrogen. E. D. McCollum and F. Daniels absorbed the nitrogen peroxide produced by means of silica gel.

A number of furnaces have been devised for the oxidation of nitrogen in the electric arc. There is K. Birkeland and S. Eyde's furnace [5] in use at Froguerikelm, Aukerlokken, Notodden, Svaelgfos, Lienfos, and Rjukan, in Norway—hence often alluded to as the Norwegian process—and at Soulom, Pyrenees ; J. von Kowalsky and I. Moscicky's furnace in use at Chippis in Switzerland ; O. Schönherr's furnace used at Christiansand, and Saaheim, in Norway, and also in Germany ; and H. Pauling's furnace, in use at Patsel, Innsbruck ; Gelsenkirchen, Westphalia ; Mulderstein, Saxony ; Roche de Rame, France ; Legnano, Milan ; Nitrolee, U.S.A. ; E. K. Scott's, P. A. Guye's, and J. S. Island's furnaces have not yet passed the experimental stages. Many others have been patented, but have not succeeded in making their way.

In **K. Birkeland and S. Eyde's furnace,** the arc between the electrodes is maintained by an alternating current of about 5000 volts and 50 periods per second, and is spread by a strong magnetic field into two semicircular discs of flame at right angles to the axis of the electrodes. The sheets of flame alternately rise and break with great rapidity in the upper and lower half of the reaction chamber. The impression on the eye is that of a steady circular sheet of flame about 1·8 metres in diameter. The electric flame is produced in a flat box of refractory material which does not attain a temp. of 1000° and is surrounded by an iron shell. The refractory lasts from 4 to 6 months. The walls of the refractory material, Fig. 60, are perforated with small openings through which air enters the reaction chamber, and impinges on the flame. The air was formerly forced through the furnace ; it is now aspirated into the furnace. A peripheral channel in the reaction chamber allows the products of the combustion to be carried away. The bevelled poles of the electromagnet are imbedded in the lining of the furnace ; the coils of the electromagnet are just outside the iron shell ; and the magnet is fed by a direct current. The electrodes are U-shaped copper tubes, cooled by a rapid current of water passing through them. They are replaced about every 3 weeks. The temp. of the flame is estimated to be 3000°–3500° ; and the temp. of the escaping gases is 800°–1000°. They then pass from the furnace into boilers used for steam-raising ; and are then led at about 250° to cooling chambers where the temp. is reduced to about 50°. The gases pass from the coolers to the absorption towers—usually 3 or 4. These towers are made of Norwegian granite ; they are about 23 metres high, and are filled with pieces of quartz. The gases enter at the bottom of the first tower and alternately top and bottom of succeeding towers. Dil. nitric acid trickles down the first two or three towers, and water down the last one. The acid from the first tower is the most conc. being about 30 per cent. HNO_3, and that taken from the three succeeding towers is respectively 20, 10, and 5 per cent. The acid is transferred from one tower to the preceding one of the series. The gas from the fourth tower enters a similar absorption tower through which a soln. of sodium carbonate containing 2 per cent. sodium hydroxide percolates. Sodium nitrate and nitrite are formed. The plan of the plant is illustrated by Fig. 62.

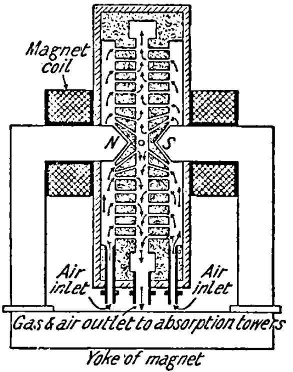

FIG. 60.—K. Birkeland and S. Eyde's Furnace (Longitudinal section showing electromagnets and reaction chamber).

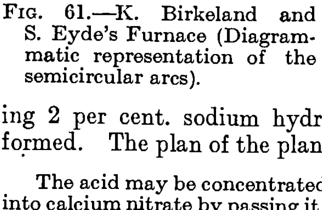

FIG. 61.—K. Birkeland and S. Eyde's Furnace (Diagrammatic representation of the semicircular arcs).

The acid may be concentrated by evaporation in special towers ; or it may be converted into calcium nitrate by passing it over limestone. The soln. of calcium nitrate is evaporated until it contains about 13 per cent. of available nitrogen when it is solidified rapidly by passage over cooled rollers. The calcium nitrate or rather basic calcium nitrate has been called *Norwegian saltpetre*, *lime-saltpetre*, and *l'azote calcaire*. The soln. of sodium nitrate and nitrate may be evaporated and sold for use in making sulphuric acid, or the nitrite may be obtained in crystals for use in dye-making. The problems connected with the absorption towers have been discussed by F. Förster and co-workers, J. A. Hall and co-workers, G. N. Lewis and A. Edgar, J. R. Partington and L. H. Parker, W. G. Schaposhnikoff, E. S. Burdick and C. L. Freed, G. Lunge and E. Berl, M Bödenstein, E. K. Rideal, G. W. Todd, M. Oswald, etc. Modifications have been devised by O. Meister and co-workers, A. A. Naville and P. A. and C. E. Guye, A. Schlösing, I. Moscicky, F. Bergius, O. Engels and F. Dürre, Det Norsk Hydroelektrisk Kuaelstofaktieselskab, etc.

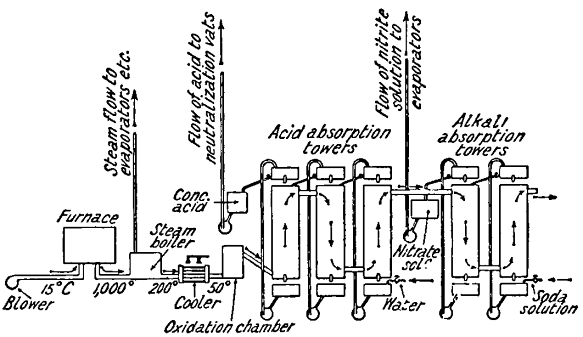

Fig. 62.—Diagrammatic Plan of Plant for the Fixation of Nitrogen by Oxidation.

In **J. von Kowalsky and I. Moscicky's furnace,** the reaction chamber is water-cooled, and the arc revolves under the influence of a powerful magnetic field, Fig. 63, with the lines of force parallel to the common axis of the electrodes. The revolving arc practically fills the working space between the electrodes. In the diagrammatic representation, Fig. 63, the air enters at *A* ; and flows past the arc *B* into the cooled chamber, *C*, and passes through *D* on to the absorption towers. The arc is maintained between the high potential electrode, *E*, and the earthed neck of the furnace *F*. As shown in the diagram, some air can enter the chamber without passing through the arc ; this is considered to be a source of weakness.

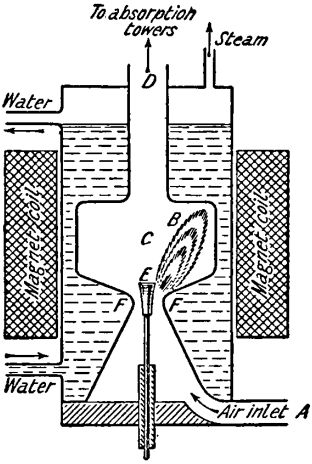

Fig. 63.—Diagrammatic Representation of J. von Kowalsky and I. Moscicky's Furnace.

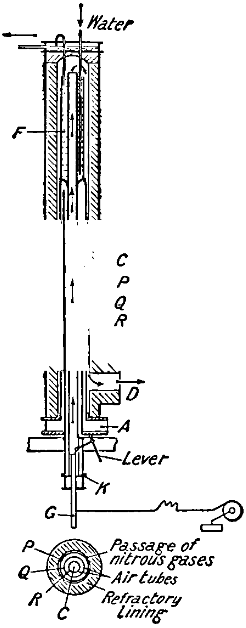

Fig. 64.—O. Schönherr's Furnace.

In **O. Schönherr's furnace,** a long slender arc is developed in the axis of an iron tube through which a current of air is forced. The arc is established by imparting a whirling motion to the air. The arc is struck by touching the iron electrode *G* against the inner tube. The air enters at *A*, and passes upwards between the steel tubes *P* and *Q*, and then downwards between *Q* and *R*. The air is thereby pre-heated before it enters the hot reaction chamber through the opening *K* arranged tangentially so as to give a whirling motion to the upward current of air in the reaction chamber *C*. The upper part of this chamber *C* is cooled by the water-jacket *F*. The reaction chamber *C* serves as one electrode, the other electrode *G* is water-cooled, and insulated from the furnace. The nitrous gases pass out of the reaction chamber *viâ* the annular space which separates the tube *P* from the refractory lining, and from *D* to the absorption towers. The process was discussed by F. Kodera and co-workers.

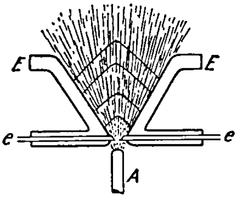

FIG. 65.—The Electrodes and Arc of H. Pauling's Furnace.

In **H. Pauling's furnace,** the arc is formed between hollow, cast-iron, or, as recommended by E. Rossi, water-cooled electrodes bent in the form of two horns *EE*, Fig. 65 ; and an arc is struck by means of the kindling blades *ee*. The air-blast from *A* forces the arc upwards and fan-wise along the inclined electrodes when it is extinguished, and a new arc follows at every half cycle of the alternating current. The arc often attains a height of three feet, the preheated air enters the reaction chamber *viâ A*, Fig. 66, and the products of combustion leave that chamber *viâ B*. One furnace with two arcs in series is placed in each leg of a three-phase current supply. There is an arrangement for momentarily supplying the special current necessary for kindling the arc.

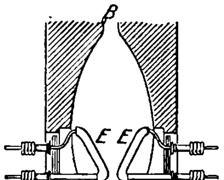

FIG. 66.—Vertical and Horizontal Sections of H. Pauling's Furnace.

In **E. K. Scott's furnace,** three horn-shaped electrodes are set at an angle of 180°, and with sides inclined towards each other at an angle of 30° from the vertical, and with intermediate refractory material, so as to form a six-sided conical space with its apex at the bottom. A blast of air is projected through the space where the electrodes converge, and bafflers are placed to force it to pass through the arc. With a 3-phase current of 60 periods, a combined arc of 360 separate flames per second is flared out by the air current. A tubular boiler placed directly above the arc cools the escaping gases from about 1000° to about 250°, and utilizes the waste-heat. In **J. S. Island's furnace,** there is a circular revolving electrode moving within a fixed annulus which forms the other electrode ; the air enters the annules, passes through the arc ; then into cooling coils, and thence to the absorption chambers.

Summaries of the patent literature or bibliographies have been made by R. H. Hosmer [6] and S. C. Stuntz. Many others have written on the subject.[7] There are also a number of brochures or books on the subject : P. Vageler, *Die Bindung des atmosphärischen Stickstoffs in Natur und Technik,* Braunschweig, 1908 ; E. Donath, *Die technische Ausnutzung des atmosphärischen Stickstoffes,* Leipzig, 1907 ; F. von Lepel, *Die Bindung des atmosphärischen Stickstoffes insbesondere durch elektrische Entladungen,* Greisswald, 1903 ; W. Schneidewind, *Die Stickstoffquellen und die Stickstoffdüngung,* Berlin, 1908 ; *Weitere Versuche über die Wirkung verschiedener Stickstoffformen aus den Jahren* 1908–1911, Berlin, 1912 ; A. König, *Ueber die Oxydation des Stickstoffes im gekühlten hochspannungsbogen bei Minderdruck,* Halle, 1908 ; K. W. Jurisch, *Salpeter und sein Ersatz,* Leipzig, 1908 ; R. Huber, *Zur Stickstofffrage,* Bern, 1908 ; G. Brion, *Luftsalpeter seine Gewinnung durch den elektrischen Flammenbogen,* Berlin, 1912 ; T. Pfeiffer, *Stickstoffsammelnde Bakterien,* Berlin, 1912 ; A. Perlick, *Die Luftstickstoff Industrie in ihrer volkswirthschaftlichen Bedeutung,* Leipzig, 1913 ; J. Knox, *Fixation of Atmospheric Nitrogen,* London, 1914 ; J. R. Partington and L. H. Parker, *The Nitrogen Industry,* London, 1922 ; T. H. Norton, *Utilization of Nitrogen,* Washington, 1912 ; P. H. S. Kempton, *Industrial Nitrogen,* London, 1922 ; W. Niiranen, *Ueber die analytische Bestimmung von Stickstoffoxyden* *und die Gültigkeit der Massenwirkungsgesetzes bei der Stickstoffsverbrennung in der Hochspannungsflamme,* Leipzig, 1907; P. A. Guye, *La fixation de l'azote et l'électrochimie,* Paris, 1906; J. C. de Ruijter de Wildt, *Wissenschaftliche Beiträge zur Literatur; I. Kolloidale Lösungen. II. Biologische und elektrochemische Bindung des atmosphärischen Stickstoffs,* Rhenen, 1906; O. Scheuer, *Recherches sur la préparation de oxydes d'azote au moyen de décharges à haute tension,* Genf, 1905; B. Waeser, *Die Luftstickstoffindustrie,* Leipzig, 1922; London, 1926.

The entrapping of nitrogen during oxidations in air.—M. Laroche[8] observed that no nitric acid is formed when a mixture of nitrogen and oxygen, confined over potash-lye and mercury, is exposed to 50 atm. press. F. Kuhlmann detected no nitric acid in a mixture of oxygen and nitrogen which had been passed through a red-hot tube, alone or in presence of platinum or platinum-black, or in moist or dry manganese dioxide. H. Davy, however, obtained nitric acid when a platinum wire is heated electrically to its m.p. in a mixture of nitrogen, oxygen, and hydrogen; F. Haber and J. E. Coates, and F. Fischer and H. Marx observed the formation of nitric oxide at white-hot surfaces in air; and the Westedeutsche Thomasphosphatwerke proposed to make nitrogen peroxide by passing air and steam through a thin-walled porcelain tube at 1600°. The diffusion of the hydrogen so formed was hastened by raising the internal press. of the gases, and lowering the press. of those outside. E. Rossi observed that some nitric acid was formed when a Nernst's filament is heated in air. J. Priestley, A. B. Fourcroy, A. Séguin, L. N. Vauquelin, and H. Cavendish noted that the water, formed by the combustion of hydrogen in oxygen mingled with nitrogen, sometimes contained nitric or nitrous acid. The French chemists considered that slow combustion was the only means of preventing the development of the acid. H. Cavendish, however, showed that when the combustion was rapid, say by detonation, the water was free from acid, and that nitric acid was formed when the oxygen predominated. N. T. de Saussure said that the freedom from nitric acid in the former case is only apparent because ammonia is simultaneously formed and this neutralizes the acid. A. Wolokitin obtained practically no oxidation during the combustion of hydrogen in air at ordinary press., but at 20 atm. press., 0·3 mol of nitric oxide was formed per 100 mols of water. H. Tominaga observed that the oxyhydrogen flame is not to be regarded as a mere source of heat because the water vapour is dissociated, forming nitric oxide. By passing a mixture of hydrogen (1·8–6·0 parts) and nitrogen (one part) at press. up to 30 atm. on to an oxyhydrogen flame with a porcelain jet, approximately equal parts of ammonia and nitric oxide were formed. Ammonium nitrate is produced when a stream of hydrogen or hydrocarbon is burnt slowly in air, and the condensed water spontaneously evaporated. R. Bunsen also noticed the formation of nitrogen oxides when electrolytic gas is exploded with air, and K. Finckh measured the proportion of nitric oxide formed when different proportions of electrolytic gas and air are exploded—*vide* **1**, 3, 7; and M. Berthelot determined the amount formed when the gases are burnt at different press. in a bomb calorimeter. E. A. Grete and P. Zöller, L. I. de Nagy Ilosva, W. Hempel, J. Pintsch, H. Kolbe, and A. W. Hofmann also noted that during the combustion of hydrogen in air, a little nitrogen is entrapped so to speak, during the oxidation, and some nitric acid is formed. S. Nagihin found that nitric acid is formed in the flame of an ordinary laboratory gas burner. A similar result was obtained by H. B. Jones, R. Böttger, A. Figuier, A. von Bibra, J. D. Boeke, A. W. Hofmann, A. R. Leeds, G. Defren, C. Wurster, E. Cramer, J. Pintsch, and L. T. Wright, during the combustion of coal gas in air; in the combustion of alcohol, wax, coal-gas, and other organic compounds in air; F. Haber and J. E. Coates, in the combustion of carbon monoxide, ethylene, and hydrogen; L. T. Wright, in the combustion of ammonia in air; and M. Berthelot, and F. C. A. Stohmann, during the combustion of nitrogenous substances.

In 1878, J. P. Rickman described an apparatus for the oxidation of nitrogen by heating a mixture of coke and a fixed base in contact with air. L. Hackspill and A. Conder observed nitric acid was formed in the manufacture of carbon dioxide during the combustion of coke, containing nitrogen; and F. Häusser, and W. A. Bone and co-workers, during the combustion of carbon monoxide under high press. in the presence of nitrogen. H. A. Humphrey devised an apparatus for exploding under press. an explosive mixture of gases containing oxygen and nitrogen under conditions to give the best yields of nitric oxide. The subject was also discussed by F. Haüsser, and C. J. Goodwin. O. Brunier entrapped nitrogen as oxide by burning oil or gas fuel under water or lime-water. M. Berthelot, and W. Hempel observed the formation of nitric acid during the combustion of carbon, or sulphur in oxygen with 8 per cent. of nitrogen contained in a calorimeter bomb, but was formed in the combustion of iron or zinc; but L. I. de Nagy Ilosva obtained nitrous oxide by using iron at 190°–250°. H. Kämmerer, and A. Müntz and E. Aubin observed nitric acid was formed during the combustion of magnesium in air; and J. F. Heller, A. R. Leeds, C. F. Schönbein, and M. Zabelin observed its formation during the slow oxidation of phosphorus; and M. Berthelot, when ether is exposed to light and air. F. Häusser devised a process for making nitric acid by detonating ordinary coal gas, or coke-oven gas mixed with an excess of air, or air enriched with oxygen, in a bomb under press.—say 5 atm. The gases are cooled rapidly after the explosion, and the 0·3–0·6 per cent. of nitric oxide formed recovered from the products by a train of absorption towers. The apparatus is continuous, fifteen explosions being produced per minute. Modifications were suggested by J. Görlinger, H. Nöh, and H. Woll. O. Dobbelstein studied the costs when coke-oven gas is employed. O. Bender proposed to burn the natural gas of Transylvania under press. in modified Bunsen's burners, and to recover the nitric oxide from the products of combustion. F. Gerhardt observed the production of nitric oxide in the combustion of the gases in gas-engines.

W. T. David and co-workers showed that ultra-red radiation hastens the combustion of mixtures of carbon monoxide or ethane and air or oxygen provided that the radiation is of a kind which is absorbed by the combustible gas, or nitrogen is present as a constituent of the inflammable mixture. The sympathetic oxidation of nitrogen which occurs indicates that nitrogen plays some part in the process of combustion. W. T. David and co-workers assume that during the combustion there is some kind of temporary association or interplay between the nitrogen molecules and those of the combustible gas which tends to retard combustion; and that the association is to some extent inhibited when the molecules of the combustible gas acquire vibratory energy by the absorption of the ultra-red radiation, with a consequent increase in the rate of combustion.

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§ 32. Nitrogen Oxides—Nitrous Oxide or Hyponitrous Oxide

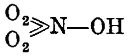
There are five oxides of nitrogen. Three of these by composition can be regarded as anhydrides of acids. Thus:

Nitrous oxide . . .	N_2O	(Hyponitrous acid . . .	$H_2N_2O_2$)
Nitric oxide	NO	(Nitrohydroxylaminic acid .	$H_2N_2O_3$)
Nitrogen trioxide . . .	N_2O_3	Nitrous acid	HNO_2
Nitrogen peroxide or tetroxide	$NO_2(N_2O_4)$	Nitric acid	HNO_3
Nitrogen pentoxide . .	N_2O_5		

N_2O is sometimes called *nitrogen monoxide;* NO, *nitrogen dioxide;* N_2O_3, *nitrogen trioxide;* N_2O_4, *nitrogen tetroxide;* and N_2O_5, *nitrogen pentoxide.* If so, NO_2, the allotropic form of N_2O_4, cannot be called nitrogen dioxide. It is doubtful if *hyponitrous acid* is the acid of nitrous oxide regarded as an anhydride; and still more doubtful if *nitrohydroxylaminic acid—vide supra—*is the acid of nitric oxide regarded as an anhydride. So far as mere composition goes, however, a mol of these oxides plus a mol of water furnishes the acids in question. Hyponitrous acid is an isomer of *nitramide*, or *nitroxyl amide.* The individuality of higher oxides or acids is not so well established.

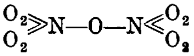
P. Hautefeuille and J. Chappius[1] found that the silent electrical discharge in a mixture of oxygen and nitrogen at a low press. does not form ozone: but M. Berthelot, and P. Hautefeuille and J. Chappius observed that a spark or powerful silent discharge produces *une acide pernitrique*, which is decomposed into nitrous or nitric acid by the attendant rise of temp. Consequently, the ozone produced by the action of the electric discharge on dry air is mixed with pernitric acid. The formation of the latter compound is limited, like that of ozone, and the maximum corresponding with a given temp. may be determined from the diminution of press. Moreover, when the maximum is reached, the pernitric acid undergoes periodic retrogradation and re-formation as already observed in the case of ozone. This decomposition of the pernitric acid into oxygen and nitric acid also causes the decomposition of the admixed ozone, even at press. above 100 mm., although ozone unmixed with pernitric acid does not undergo retrogradation at these press. This result is probably due to the development of heat accompanying the decomposition of the pernitric acid. At ordinary press. in presence of certain proportions of nitric acid, the ozone and pernitric acid are not re-formed, but under low press. they are again produced. The amount of pernitric acid formed depends more on the temp. than on the relative proportions of oxygen and nitrogen; and to obtain a good yield the operation should be conducted at a low temp. The maximum quantity produced at 15° under a press. of 600 mm. is about 30 per cent. by weight. The formation and decomposition of the pernitric acid may be traced with the aid of the spectroscope. The absorption spectrum observed by J. Chappius is characterized by fine lines in the red, orange, and green; the most characteristic ones correspond with wave-lengths 6680–6650, and 6280–6250. Water or a trace of moisture immediately causes the spectrum to disappear, and the substance is therefore an anhydrous compound capable of forming an acid. The mixture of ozone and the new substance is changed by heat, yielding nitric acid. At ordinary temp. the change is slow, and a period of from 24 to 48 hrs. occurs after the disappearance of the dark lines of the new substance, before those of the nitric acid make their appearance. On cooling a mixture of oxygen, nitrogen, and ozone charged with the vapours of pernitric acid to —23°, a small quantity of a highly volatile crystalline powder is condensed, but cannot be isolated. An indirect analysis gave for the ultimate composition: NO_3, or N_2O_6, which L. Spiegel represented by the graphic formula $NO_2.O.O.NO_2$—**nitrogen hexoxide.** E. Warburg and G. Leithäuser obtained an analogous product by the action on ozone of nitrous gases. F. Raschig *assumed* that an unstable mixture of nitrogen hexoxide and nitrogen heptoxide is formed when nitric oxide acts on a large excess of oxygen. This could not be isolated. According to D. Helbig, when a series of electrical discharges is sent through liquid air, a flocculent, unstable, greenish substance is formed which decomposes in air at a low temp. giving off reddish vapours. The decomposition is sometimes explosive. The composition corresponds with that of nitrogen hexoxide. When suspended in the excess of liquid air, nitrogen hexoxide bears a strong resemblance to precipitated chromic hydroxide, but when the air has been removed by evaporation under reduced press. it forms a slightly blue, amorphous powder. It melts at —111°, and at the same time assumes a deep azure colour, which persists after the liquid has been resolidified by immersion in liquid air. The fused oxide decomposes, yielding nitric oxide, which is also evolved when the liquid is placed in a vacuum. F. Raschig obtained green flocks of what he considered to be the same compound by passing dry nitric oxide into liquid oxygen, and allowing the excess of oxygen to evaporate. E. Müller showed that neither the composition nor the m.p. is constant, and inferred that the green substance is a mixture. The colour may be exactly imitated by dipping a test-tube containing liquid air in liquid nitrogen trioxide, and, after a frozen layer has been formed, in liquid nitrogen tetroxide. The two layers of blue and yellow give a green which is exactly like that of the supposed hexoxide. According to R. L. Hasche, the green solid obtained by bubbling nitric oxide through liquid oxygen, or by the action of air on solid nitric oxide at the temp. of liquid oxygen, is a **nitrosonitrogen trioxide,** $(N_3O_4)_n$. It decomposed above the b.p. of oxygen to the blue oxide, N_2O_3, of D. Helbig. F. Raschig's formula is considered not to be correct. Assuming, because of its instability and its instantaneous formation, that the green oxide is a peroxide of polymerized nitric oxide, its formation may be explained as follows: $O.O+2(NO.NO.N:O)\rightarrow O:N.NO.O.O.NO.NO.N:O$. The phenomena observed in the oxidation of nitric oxide may be explained by the assumption of similar intermediate compounds, *viz.*, at higher temp., O : N.NO.O.O.NO.N : O, formed by the oxidation of $(NO)_2$, and, in the gaseous state, O : N.O.O.N : O, formed by the oxidation of NO.

By treating soln. of the alkali nitrates with sodium dioxide, E. Pinerua-Alvarez claimed to have made alkali salts of true **pernitric acid,** HNO_4. Thus, 160 grms. of sodium dioxide were gradually added to a well-cooled soln. of 100 grms. of potassium nitrate in 200 c.c. of water, and 1200 grms. of alcohol. An amorphous precipitate of **potassium pernitrate,** KNO_4, was obtained on adding 1200 grms. of alcohol, and rapidly filtering: $KNO_3+Na_2O_2+H_2O=KNO_4+2HaOH$. More pernitrate was removed by evaporating the filtrate. The salt is decomposed by water or acids producing hydrogen dioxide or oxygen. F. Raschig reported pernitric acid to be formed by the interaction of nitrogen peroxide and hydrogen dioxide. J. Schmidlin and P. Massini found that the product did not oxidize manganous salts, and they therefore suggested that it is not a true per-acid, but rather *nitrous hydroperoxide.* I. Trifonoff obtained pernitric acid by the action of hydrogen dioxide on an acidified soln. of a nitrite. Above 70°, the product decomposes rapidly; it liberates bromine from potassium bromide. The formula is represented by $NO_2.O.O.NO_2$ plus nH_2O; and the reaction by which it is formed, by $2HNO_2+3H_2O_2+(n-1)H_2O=N_2O_6 \cdot nH_2O+3H_2O$. Aniline, benzene, toluene, xylene, and the aliphatic hydrocarbons are coloured yellow by pernitric acid. F. Pollak established the formation of pernitric acid from nitric acid and hydrogen dioxide in the presence of potassium bromide. At 15°, the initial velocity of bromine separation is proportional to the first power of the nitric acid conc. and the potassium bromide conc. The exponent for the hydrogen dioxide, however, is approximately 0·80. Different reactions are found to predominate if the same relative quantities of reactants are present, but the total conc. is different. The influence of light is also a disturbing factor. *Vide* silver peroxynitrate, **3.** 22, 23, for the possible formation of a **silver pernitrate** during the electrolysis of an aq. soln. of silver nitrate. E. Mulder and J. Heringa suggested that silver peroxynitrate, $3Ag_2O_2 \cdot AgNO_3$ (*q.v.*), is possibly a salt of *hypernitric acid,* HNO_5, or $HO \cdot NO_4$, *i.e.* of the anhydride, *nitrogen enneaoxide,* N_2O_9:



$$\begin{matrix}O_2\\O_2\end{matrix}\!\gg N-OH$$

Hypernitric acid.



$$\begin{matrix}O_2\\O_2\end{matrix}\!\gg N-O-N\ll\!\begin{matrix}O_2\\O_2\end{matrix}$$

Nitrogen enneaoxide.

E. P. Alvarez[2] found that the pernitrates react with soln. of lead acetate (white precipitate), silver nitrate (white precipitate), mercurous nitrate (white precipitate with rapid decomposition), mercuric chloride (red precipitate), copper sulphate (blue precipitate), zinc and cadmium sulphates (white precipitate), bismuth nitrate (white precipitate), gold chloride (slight effervescence and escape of oxygen), manganous chloride (pink precipitate), nickelous chloride or sulphate (greenish-white precipitate), cobaltous nitrate and chloride (pink precipitate), ferrous sulphate (green or bluish-green precipitate), ferric chloride (red ferric hydroxide), and alkaline earth chlorides (white precipitates). The precipitates are all per-salts of the bases in question.

In 1772, J. Priestley[3] compared the action of fixed air (carbon dioxide) and of nitrous air (nitric oxide) on moist iron, and observed no sensible change with the former gas, but the latter gas was "transformed into a species of air in which a candle burned quite naturally, and freely, and which is yet in the highest degree noxious to animals insomuch that they die the moment they are put into it; whereas, in general, animals live with very little sensible inconvenience in air in which candles have burned out." He later showed that the candle burns in the new gas with an enlarged flame; and that whereas if liver of sulphur be substituted for iron, the conversion of the nitric oxide to the new gas is shortened from 6 to 8 weeks to 24 hrs.—especially if the liver of sulphur be kept warm. He also found that the same gas is formed when zinc or tin is dissolved in spirit of nitre (nitric acid). He called the new gas *dephlogisticated nitrous air ;* it is now known as **nitrous oxide,** N_2O. In 1793, J. R. Deiman and co-workers prepared this gas by heating ammonium nitrate, and showed that it is a lower oxide of nitrogen than nitric oxide. In 1800, H. Davy made an extensive investigation on the gas and discovered its intoxicating qualities, from which it obtained its name *laughing gas.*

The preparation of nitrous oxide.—Nitrous oxide is not easily formed by direct union of oxygen and nitrogen. M. Berthelot and H. Guadechon obtained none under the influence of ultra-violet light. E. Warburg and G. Leithäuser found that when a mixture of oxygen and nitrogen is passed through an ozonizing tube, nitrous oxide, and nitrogen pentoxide are formed; if the mixed gas is sparked between platinum electrodes, nitrous oxide and nitrogen peroxide are formed; and when exposed to the alternating arc of high tension, nitric oxide and nitrogen peroxide are formed. According to D. L. Chapman and co-workers, nitrous oxide is slowly formed when an electric discharge is passed through nitrogen at a low press. in a quartz tube into the walls of which oxygen has previously been driven by means of the discharge. C. Matignon argued from thermodynamical considerations that the production of nitrous oxide ought to be possible by the direct union of oxygen and nitrogen at 3000° and 3000 atm. Unless the gas was rapidly removed from the hot zone and cooled, the yield would be only 0·1 per cent. According to R. Pictet, and K. A. Söderman, the nitrogen-oxygen flame produced electrically or by other means shows spectroscopically that nitrous oxide is present in some parts ; and by rapid cooling, it is possible to obtain a 25 per cent. yield—*vide supra,* the fixation of nitrogen.

Nitrous oxide is commonly made by the process of J. R. Deiman and co-workers, *viz.*, by heating anhydrous, neutral ammonium nitrate to 170°–260°. The gas can be collected over water, brine, or mercury. The ammonium nitrate used should be free from chlorine. According to E. Thilo, most of the commercial ammonium nitrate is not sufficiently purified for use in making the gas. Any nitric oxide which might be formed can be removed by passing the gas through a soln. of ferrous sulphate. P. Cazeneuve said that the gas may retain an irritating odour even after its passage through a soln. of ferrous sulphate, and of sodium hydroxide. He attributed this to the presence of a little hyponitrous acid, and it was removed by shaking the gas several times with a soln. of ferrous sulphate, or allowing it to stand 24 hrs. in a gas-holder. P. Villard said that nitrous oxide of a very high degree of purity is obtained by converting the gas first into the hydrate, and then allowing the hydrate to decompose. P. Cazeneuve explained the explosion which sometimes take place in the preparation of the gas by the fact that the decomposition of ammonium nitrate is an exothermic reaction, and that the large quantity of heat thus liberated added to that directly applied, is capable of causing the sudden decomposition of the whole mass of the salt. The process is often slow in beginning on account of the contained moisture, and hence the operator is apt to apply undue heat at first. Therefore, the salt should previously be dried in a capsule at a temp. below 200°, and the retort should be heated slowly until the disengagement of gas begins, when only a very gentle heat will be required, and the operation should not be pushed too far towards the end. V. H. Veley has studied the way the salt decomposes when heated—*vide* **2**. 20, 38. According to A. P. Lidoff, the gas as usually prepared contains appreciable quantities of nitrogen, nitric oxide, and other impurities, and he recommended the following process :

> A tube of difficultly fusible glass, sealed at one end, is filled with a mixture of 3 parts of dry sea-sand and 2 parts of ammonium nitrate dried at 105°, which is kept in position by an asbestos plug ; the end of the tube is closed by a cork through which passes a delivery tube with a tap. A small aluminium box, fitted with a thermometer and serving as an air-bath, is arranged to slide along the tube. The best temp. to employ is 260°–285°, and the back end of the tube is first heated ; when all the air has been expelled from the tube, the gas is passed, first through aqueous ferrous sulphate or alkaline sodium sulphide soln.,

and then through an emulsion of dry ferrous sulphate in conc. sulphuric acid ; it is then pure and dry.

V. H. Veley found that the reaction is accelerated by inert substances like ground-glass, pumice, silica, barium sulphate, graphite. P. Grouvelle used a mixture of potassium nitrate and ammonium chloride (3 : 1) in place of ammonium nitrate. According to A. M. Pleischl, the product is a mixture of chlorine, nitrogen, and nitric oxide with a little nitrous oxide, but E. Soubeiran said no nitrous oxide is thus produced. W. Smith and W. Elmore patented a mixture of dried commercial sodium nitrate, potassium nitrate, and ammonium sulphate (17 : 20 : 13–14), which yields nitrous oxide when heated to about 230° for the greater part of the reaction, and finishing at 300°. The apparatus should be arranged so that the condensed water does not drip back into the retort. The gas should be washed in a dil. acid, and dil. alkali-lye. W. Smith found that in this reaction, as the temp. rises ammonia is first evolved : $(NH_4)_2SO_4=NH_3+(NH_4)HSO_4$, the ammonium hydrosulphate begins to react with the sodium nitrate—possibly forming NH_4NaSO_4 and HNO_3 ; but this change proceeds slowly, and the ammonia reacts with the liberated nitric acid, forming ammonium nitrate. At about 240°, the ammonium sodium sulphate reacts with sodium nitrate, forming sodium sulphate and ammonium nitrate which then decomposes : $NH_4NO_3=N_2O+2H_2O$. If the temp. falls below the point of evolution of nitrous oxide—about 240°—the ammonium nitrate formed cannot decompose into nitrous oxide. K. A. Hofmann and G. Buhk said that nitrous oxide mixed with very little nitrogen and nitric oxide can be conveniently made at ordinary temp. by the action on copper of 14 grms. of sodium nitrite, 22 grms. of ammonium chloride, sulphate, or hydrocarbonate in 200 c.c. of water. The 1025 c.c. of gas contained 845 c.c. of nitrous oxide, 81 c.c. nitric oxide, and 99 c.c. of nitrogen. The reaction is due in the first place to the reduction by the copper of free nitrous acid formed by hydrolysis of ammonium nitrite (produced by double decomposition of the sodium nitrite and ammonium salt), $2HNO_2+Cu=2NO+Cu(OH)_2$. The cupric hydroxide dissolves in the ammonia (a blue colour appears on the surface of the copper), and is reduced by copper to the cuprous form. The cuprous oxide then reduces the nitric oxide further to nitrous oxide, $2NO+Cu_2O=N_2O+CuO$. The free nitrogen must be formed by the normal decomposition of ammonium nitrite into nitrogen and water. Magnesium nitrite behaves in a similar manner with copper, but, since it is much less hydrolyzed than ammonium nitrite, the reaction proceeds at only about one-sixtieth of the rate.

In the original process employed by J. Priestley for preparing this gas, nitric oxide was reduced by means of iron or liver of sulphur ; F. Kuhlmann reduced that gas with hydrogen sulphide, dry or moist liver of sulphur, iron- or zinc-filings, moist iron sulphide, or sulphur dioxide—gas or aq. soln. ; J. L. Gay Lussac, a soln. of stannous chloride, or ammonia ; and G. Lechartier, an alkaline soln. of pyrogallol. Nitrous oxide is formed in the reduction of nitric oxide by sulphur dioxide, for if the mixed gases (2 : 1) be allowed to stand over water for some hours, J. Pelouze observed the formation of nitrous oxide. J. Gay found that a soln. of nitric oxide in ferrous sulphate is readily reduced to nitrous oxide by, say, ferrous oxide. J. Donath obtained the gas by the action of an alkaline soln. of a copper salt on hydroxylamine chloride. E. Cardoso and E. Arni, by the action of a sat. aq. soln. of sodium nitrite on hydroxylamine in vacuo, and subsequently fractionating the washed solid ; and G. Oesterheld, by the electrolytic oxidation of an alkaline soln. of hydroxylamine at a platinum anode. It is here assumed that hyponitrous acid is first formed, $2NH_2OH+O_2=2H_2O+H_2N_2O_2$; and that the acid breaks down into nitrous oxide and water : $H_2N_2O_2=N_2O+H_2O$. The nitrogen simultaneously produced cannot be derived from ammonium nitrite because no ammonia is present, and because there can be no oxidation of hydroxylamine to nitrous acid at the low anode potential which was maintained. The simplest explanation is that the nitrogen is due to the reaction between hydroxylamine and nitroxyl which is the first oxidation product, $O:NH+NH_2OH=N_2+2H_2O$. A. Angeli has observed the same reaction when nitroxyl splits off from benzene sulphohydroxamic acid in presence of hydroxylamine. While two mols. of nitroxyl may combine to form hyponitrous acid or nitrous oxide and water, yet there is a quantitative evolution of nitrogen so long as there is a sufficient excess of hydroxylamine. It is also possible that nitrogen may be formed simultaneously with nitrous oxide by a different decomposition of hyponitrous acid, indicated by M. Berthelot and J. Ogier, A. Hantzsch and L. Kaufmann, and P. C. Ray and A. C. Ganguli, perhaps $5H_2N_2O_2=4H_2O+2HNO_3+4N_2$; A. Thum, by the decomposition of a soln. of hyponitrous acid. M. Coblens and J. K. Bernstein found nitrous oxide but not ammonia is formed when silver hyponitrite is added to an acid soln. of titanous chloride. E. Frémy found that a soln. of nitrous acid or a nitrite is reduced to nitrous oxide by warm sulphurous acid; W. Zorn, by sodium amalgam, or stannous chloride; O. von Dumreicher, by ferrous hydroxide; and V. Meyer, and P. A. Guye and S. Bogdan, by hydroxylamine sulphate in aq. soln.—conc. soln. require heating, dil. soln. want boiling. J. Priestley reduced nitric acid to nitrous oxide by zinc or tin. N. A. E. Millon used nitric acid of sp. gr. 1·217 with zinc, tin, or copper at —10°. T. von Grotthus, and A. M. Pleischl said the gas by the zinc-reduction process is fairly pure. H. Bassett recommended a mixture of sulphuric acid (1 vol.), nitric acid (2 vols.), and water (3 vols.), and found nitrous oxide is given off in the cold when tin is used. H. Schiff used the proportions 1 : 1 : 9–10 respectively with zinc. J. J. Acworth found that in the reaction between copper and nitric acid, the resistance of much cupric nitrate favours the production of nitrous oxide. F. Mareck also reduced nitric acid with zinc. E. Frémy reduced nitric acid with sulphur dioxide; and J. L. Gay Lussac reduced aqua regia by stannous chloride. A soln. of stannous chloride in hydrochloric acid and some crystals of potassium nitrate, heated on a water-bath, gave off nitrous oxide gas. According to G. Campari, on boiling a mixture of 5 parts of stannous chloride, 10 parts of hydrochloric acid, sp. gr. 1·21, and 0·9 part of nitric acid, sp. gr. 1·38, the evolution of nitrous oxide commences, and continues to be evolved quite regularly and in a pure state. These proportions of the ingredients should be adhered to, as otherwise the gas is evolved irregularly, and even with violent explosions. A. Quartaroli reduced nitrates with formic acid: $2KNO_3+6H.COOH=N_2O+4CO_2+5H_2O+2HCOOK$.

T. Schlösing found that some nitrous oxide is formed during the lactic fermentations of organic substances in a soln. containing nitrates; and M. E. Wollny, B. Tacke, M. W. Beyerinck and D. C. J. Minkman, and S. Suzuki observed the formation of nitrous oxide during the nitrification of organic matter by bacteria.

The physical properties of nitrous oxide.—Nitrous oxide at ordinary temp. is a colourless gas, with a faint smell and sweet taste; it also forms a colourless liquid, and a colourless solid, which, according to H. E. Behnken,[4] crystallizes in the cubic system. J. de Smedt and W. H. Keesom found the **X-radiogram** of the crystals gave a space-lattice having a unit cube with side 5·72 A.; there are four mols. in the unit cube; and the distance between two neighbouring oxygen and nitrogen atoms is 1·15 A. The early determinations of the **relative density**—1·3629 by C. L. Berthollet, and 1·614 by J. Dalton—are far from the mark. A. Leduc first gave 1·52951, and later 1·5301 with an accuracy of 0·01 per cent.; Lord Rayleigh gave 1·52951, and later 1·5297. O. von Dumreicher said that the gas has a normal density at 100°. The literature was reviewed by M. S. Blanchard and S. F. Pickering. W. G. Shilling gave for the density of the gas at 0°, 0·00197. T. Wills gave 0·9004 for the specific gravity of the liquid; and L. P. Cailletet and E. Mathias found the sp. gr., D_l, to be:

	—20·6°	—11·6°	—5·5°	—2·2°	6·6°	11·7°	19·8°	23·7°
Sp.gr., D_l . .	1·002	0·952	0·930	0·912	0·849	0·810	0·758	0·698

or, the sp. gr. of the liquid at $\theta°$ between —20·6° and +23·7° is $D_l=0{\cdot}342+0{\cdot}00166\theta+0{\cdot}0922\sqrt{36{\cdot}4-\theta}$, and for the sp. gr. of the gas, D_g, they gave:

	—28·0°	—23·5°	—12·2°	—1·5°	9·2°	20·7°	28·9°	33·9°
Sp.gr., D_g	0·0378	0·0413	0·0566	0·0785	0·1066	0·1532	0·2023	0·2650

or at $\theta°$, between $-28·0°$ and $+33·9°$, $D_\theta=0·5099-0·00361\theta-0·0714\sqrt{36·4-\theta}$. J. de Smedt and W. H. Keesom estimated the sp. gr. of the solid to be 1·55. The sp. gr. of the liquid at the m.p. is 1·299. The sp. gr. at the b.p., —89·4°, was found by L. Grunmach to be 1·2257; and P. Villard gave for the sp. gr. at the critical temp., 38·8°, 0·454 for liquid and vapour. E. d'Andréeff, and P. Villard made observations on the sp. gr. of the liquid or gas; the former gave $D_l=0·9368-0·0039\theta$. L. Meyer gave 26·7 for the mol. vol. of the liquid; and R. Lorenz and W. Herz also studied this subject. For the **weight of a litre** of the gas under standard conditions, J. J. Colin gave 1·9752 grms.; and J. Dalton, 1·614. A. Leduc, and P. A. Guye and A. Pintza, first gave 1·97788 grms., and later 1·9774 grms. J. S. Stas found the molecular weight to be 43·98, hydrogen unity. A. Naumann gave for the **molecular volume,** 4·49 (hydrogen unity). R. Lorenz and W. Herz, and G. le Bas studied the mol. vol. C. E. Guye and R. Rudy, and E. Rabinowitsch gave 36 for the mol. vol. A. Naumann found the **molecular diameter** to be 2·72 (hydrogen unity); and the mol. radius, 1·65 (hydrogen unity). E. Dorn calculated the diameter to be $1·8\times10^{-7}$ cm.; H. Sirk, $3·1\times10^{-8}$ to $4·0\times10^{-8}$ cm.; J. H. Jeans, $4·6\times10^{-8}$ cm.; J. P. Kuenen, $3·1\times10^{-8}$ cm.; S. Mokruschin, $5·8\times10^{-8}$ cm.; P. Walden, $2·9\times10^{-8}$ cm.; and A. von Obermayer, $0·32\times10^{-7}$ cm. C. J. Smith calculated the mean collision area to be $0·834\times10^{-15}$ sq. cm. For the **molecular velocity,** A. von Obermayer gave 36,250 cms. per sec. at 0°, and for the **mean free path,** 387×10^{-8} cm. J. E. Mills has discussed the inter-**molecular attraction**; M. Trautz and O. Emert, F. Braun, A. Leduc, and P. Sacerdote discussed the application of the partial press. law to mixtures of nitrous oxide with carbon dioxide, etc. R. Gans, and E. Brüche discussed the structure of the molecule of the gas.

The **viscosity** of nitrous oxide gas was found by O. E. Meyer [5] to be 0·000168; O. E. Meyer and F. Springmühl gave 0·000160; C. J. Smith, 0·0001366 at 0°, 0·0001441 at 15°, and 0·0001845 at 100°; and A. Wüllner, 0·0001353 at 0°, and 0·0001815 at 100°. T. Graham's results, 0·0001408 at 0° and 0·0001600 at 20°, were too high. A. von Obermayer gave $0·0_31249$ at —21·5°, $0·0_31606$ at 53·6°, and $0·0_31829$ at 100·3°; W. G. Shilling, $0·0_31366$ at 0°; and H. Vogel, $0·0_31362$ at 0°. W. J. Fisher obtained

	25°	141·6°	183·1°	224·4°	289·9°	413·6°
$\eta\times10^7$ . .	1498	1831	2161	2348	2610	3073

A. von Obermayer represented his results at $\theta°$ between —21·5° and 100·3° by $\eta=\eta_0(1+0·003719\theta)^{0·929}$, where $\eta_0=0·0_316586$; W. J. Fisher employed $\eta=\eta_0(0·0_41707T^{\frac{1}{2}})/(1+314T^{-1})$. J. H. Jeans gave $\eta=\eta_0(T/273)^{0·93}$. Y. Ishida gave 0·795 for the ratio of the viscosities of nitrous oxide and air. W. G. Shilling gave 286 for Sutherland's constant. F. Schuster calculated 2233 atm. for the **internal pressure.** L. L. Grunmach gave for the **surface tension,** σ, of liquid nitrous oxide, 1·74 dynes per cm. at 19·8°; 2·50, at 14·4°; 9·92, at —24°; and 26·32, at the b.p., —89·3°; and for the **specific cohesion,** $A^2=0·582$ sq. mm. at 19·8°; 0·759, at 14·4°; 2·510, at —24·0°; and 4·296, at the b.p. —89·3°. For the mol. **surface energy,** $\sigma v=2·27(43·52-\theta)$, where v is the sp. vol.; if M be the mol. wt., and D the sp. gr., $M=D\{2·27(43·52-\theta)/\sigma\}^{\frac{3}{2}}$. J. Verschaffelt represented his results between 19·8° and —24°, by $\sigma=A(1-m)^{1·333}$, where $\log A=1·945$, and m denotes the reduced temp. L. L. Grunmach's results agreed with the assumption that the mol. wt. of the liquid is the same as that of the gas. A. von Obermayer [6] gave for the **diffusion** coeff. of carbon dioxide into nitrous oxide at 0°, 0·148, and J. Loschmidt, 0·098; and for hydrogen into nitrous oxide, A. von Obermayer gave 0·535. G. Hüfner measured the rate of diffusion of the gas in water and found the coeff. to be 1·35 at 16·2°; while A. Hagenbach obtained 0·63 at 14°. H. A. Daynes measured the diffusion through rubber. T. L. Ibbs and L. Underwood studied the thermal diffusion of nitrous oxide and carbon dioxide. For the velocity of sound in nitrous oxide at 0°, A. Wüllner gave 260 metres per second; G. Schweikert, 256; and W. Heuse, 257 metres per second.

A. Kundt, E. J. Irons, and C. Bender made some observations on this subject. W. G. Shilling gave at room temp., 264·6 metres per second; at 100°, 299·0; at 200°, 334·3; at 300°, 365·4; at 400°, 393·9; at 500°, 420·3; and at 600°, 446·9. N. de Kolossowsky studied the relation between the velocity of sound, and the velocity of translation of the molecules.

According to Lord Rayleigh,[7] the ratio of the **compressibility,** pv, at half an atm. to that at one atm. press. is 1·00066; and later at 11°, he obtained 1·00327. T. Bateucas gave 0·0000978 for the compressibility at 0°; and 1·00739 for the divergence from Avogadros' rule, $1+\lambda$. Observations on the **vapour pressure** of nitrous oxide were made by M. Faraday, K. Olschewsky, W. J. Janssen, J. P. Kuenen, etc. The values for the liquid by P. Villard were 30·75 atm. at 0°, and 49·4 atm. at 20°; L. P. Cailletet gave 5·05 atm. at —60°; and 13·19 atm. at —34°. The following data for the vap. press., p atm., are by G. A. Burrell and I. W. Robertson—the values at 0°, 20°, and 40° are by H. V. Regnault:

	Solid.					Liquid.				
	−144·1°	−131·3°	−117·2°	−99·5°	−90·6°	−90·1°	−88·7°	0°	20°	40°
p .	0·00158	0·0092	0·0658	0·3948	0·8686	0·9212	1	36·08	55·30	83·37

H. V. Regnault represented his results at θ°, between —40° and 35°, by $\log p = 9{\cdot}2420206 - 5{\cdot}056207\alpha^{\theta+26}$, where $\log \alpha = 9{\cdot}9991451 - 10$; C. Antoine, $\log p = 9{\cdot}4574\{1{\cdot}46927 - 1000/(\theta+1000)\}$; and G. A. Burrell and I. W. Robertson, $\log p = -1096{\cdot}7T^{-1} + 17{\cdot}5 \log T + 0{\cdot}0005T + 4{\cdot}866$, or $\log_{10} p = -1232{\cdot}2T^{-1} + 9{\cdot}579$. J. P. Kuenen studied the vap. press. of mixtures of liquid ethane and nitrous oxide. W. Nernst gave 3·3 for the **chemical constant,** and W. Herz discussed this subject.

P. von Jolly found the coeff. of **thermal expansion** to be 0·003706. C. A. Würtz gave 0·00428 between —5° and 5°; and being unity at 0°, was found to be 1·0455 at 10°, and 1·1202 at 20°. F. Guye and L. Friedrich gave for the constants in J. H. van der Waals' **equation of state** $(p+av^{-2})(v-b)=RT$, $a=0{\cdot}00723$ (or 0·00750), and $b=0{\cdot}00189$ (or 0·00195) if taken in terms of the initial vol.; $a=3{\cdot}62\times10^6$ (or $3{\cdot}72\times10^6$), and $b=42{\cdot}3$ (or 43·4) if in mols; and $a=18{\cdot}7$ (or 192), and $b=0{\cdot}961$ (or 0·987) if in grams. W. J. Walker also discussed the equation of state.

G. Wiedemann[8] first measured the **thermal conductivity** of nitrous oxide. A. Wüllner found the constant to be $0{\cdot}0_4350$ at 0°, and $0{\cdot}0_4506$ at 100°; J. Stefan gave $0{\cdot}0_4372$ at about 10°; S. Weber, $0{\cdot}0_4353$; A. Winkelmann, $0{\cdot}0_4350$ at 0°, and $0{\cdot}0_4506$ at 100°; W. G. Shilling, $0{\cdot}0_4351$; and A. Eucken, $0{\cdot}0_43515$ at 0°, and $0{\cdot}0_42710$ at —71·8°.

F. Delaroche and J. E. Bérard[9] found the **specific heat** of nitrous oxide at constant press. to be 0·2369 between 15° and 100°; H. V. Regnault, 0·226 between 16° and 207°; and E. Wiedemann gave 0·1983 at 0°; 0·2212 at 100°; and 0·2442 at 200° at one atm. press., while at 30 atm. press., the sp. ht. was 0·278. H. N. Mercer gave 0·2185; and W. Heuse, 0·210 at 20°; 0·200 at —30°; and 0·190 at —70°. K. Scheel and W. Heuse, for the mol. heat, $C_p=9{\cdot}24$ at 20°; 8·79 at —30°; and 8·37, at —70°; and for the ratio of the two sp. hts., P. L. Dulong gave 1·253 at 20°; A. C. G. Suermann, 1·36; A. Cazin, 1·285 at 15°; A. Masson, 1·293 at 0°; T. Martini, 1·354 at 7°; G. Schweikert, 1·283 at 0°; A. Wüllner, 1·311 at 0°, and 1·272 at 100°; A. Leduc, 1·324 at ordinary temp.; J. R. Partington and W. G. Shilling, 1·302; H. N. Mercer, 1·261; and W. Heuse, 1·28 at 20°; 1·31 at —30°; and 1·34 at —70°. W. G. Shilling gave for the mol. ht. at constant vol., $C_v=6{\cdot}629+0{\cdot}00069\theta-0{\cdot}0_5241\theta^2$; and at constant press., $C_p=8{\cdot}659+0{\cdot}00677\theta-0{\cdot}0_5222\theta^2$. A. Eucken and E. Donath gave $C_p=7{\cdot}39$ for the solid at —125·25°.

Nitrous oxide gas is easily liquefied. In 1823, M. Faraday[10] heated thoroughly dried ammonium nitrate in one leg of a Λ-tube, and on cooling the other leg of the tube, obtained two liquids; one a soln. of nitrous oxide in water, and the other water in nitrous oxide. It is doubtful if J. H. Niemann prepared the liquid gas in in this way. The liquefaction by compression and cooling has been described by

G. S. Newth, M. Thilorier, L. P. Cailletet, J. H. Debray, J. O. Natterer, T. Wills, and others. Liquid nitrous oxide, contained in steel cylinders holding up to about 50 lbs. and eq. to 430 c. ft. of gas, is on the market. In 1845, M. Faraday cooled the liquid in a bath of solid carbon dioxide and ether below —100°, and obtained colourless crystals of nitrous oxide; C. Despretz found that the liquid in a silver dish in vacuo froze readily to a snow-like mass; and J. A. Natterer obtained solid, snow-like nitrous oxide by allowing the liquid to stream through a fine opening into the air. W. Ramsay and J. Shields found the **melting point** of the solid to be —102·3°. M. Faraday estimated —100°; T. Wills, —99°; J. A. Natterer, —115°; and P. A. Guye and G. Drouginine, —105·8°. For the **boiling point,** H. V. Regnault gave —87·9° at 767·3 mm.; T. Willis, —92°; L. Grunmach, —89·4° at 760 mm.; F. W. Bergstrom, —89·5°; P. A. Guye and G. Drouginine, —89·8°; W. Ramsay and J. Shields, —89·8° at 760 mm.; M. A. Hunter, —87° at 760, and —89·1° at 660 mm.; G. W. Burrell and I. W. Robertson, —88·7° at 760 mm.; and F. W. Bergstrom, —89·5°±0·2°. E. Cardoso and E. Arni found the **critical opalescence** extended from 36·0° to 36·5° and had a maximum at 63·3°. J. A. Muller gave 1·359 for the degree of polymerization in the critical state. J. Dewar gave 35·4° for the **critical temperature;** P. Villard, 38·8°; J. P. Kuenen, 36·0°; W. J. Jannssen, 36·4°; L. P. Cailletet and E. Mathias, 37·0°; and E. Cardoso and E. Arni, 36·50°. The subject was studied by W. Herz. For the **critical pressure,** J. Dewar gave 75 atm.; W. J. Jannssen, 73·07 atm.; and P. Villard, 77·5 atm.; and E. Cardoso and E. Arni, 71·65 atm. L. P. Cailletet and E. Mathias gave 0·0048 for the **critical volume,** and 0·41 for the **critical density;** P. Villard gave 0·454 for the critical density. W. Herz examined the relations of the critical constants of this oxide. S. F. Pickering gave for the best representative values T_c=309·6° K.; p_c=71·7 atm.; and D_c=0·45. L. P. Cailletet and E. Mathias gave for the **heat of vaporization,** 66·9 cals. per gram at —20°; 59·7 cals. at 0°; 43·7 cals. at 20°; and 13·5 cals. at 35°; and D. L. Hammick gave 69·4 Cals. G. A. Burrell and I. W. Robertson gave 5·626 cals. per mol. as the average heat of evaporation at about —90°. H. Crompton calculated data in agreement with L. P. Cailletet and E. Mathias's results. A. Eucken and E. Donath gave for the heat of vaporization of solid nitrous oxide 5822 cals. at —137·5°, and 5695 cals. at —113°.

J. Thomsen[11] found the **heat of formation** of gaseous nitrous oxide from its elements to be —18·32 Cals.; and M. Berthelot, —20·6 Cals. for the gas, —18·0 Cals. for the liquid; and —14·4 for the gas in aq. soln. J. Thomsen gave for (NO,N_2), 3·255 Cals. M. Berthelot and P. Vieille calculated the temp. of combustion of a mixture of nitrous oxide and cyanogen to be 3596°–4149°. J. C. Thomlinson calculated what he called the thermochemical eq. of the nitrogen contained in nitrous oxide—*vide infra.*

P. L. Dulong[12] gave for the **index of refraction** of nitrous oxide 1·000507, for white light; J. Jamin, 1·000507 for red light; H. Becquerel, for Na-light, 1·0005159; and E. Mascart, 0·0005084 for Na-light at 0° and 760 mm. If λ denotes the wave-length, the index of refraction $\mu=A(1+0{\cdot}0127\lambda^{-1})$. C. and M. Cuthbertson gave 1·00051415 for λ=477·9μμ; 0·00051145 for λ=520·9μμ; 0·00051000 for λ=546·1μμ=0·00050848 for λ=579·0μμ; and 0·00050544 for λ=670·8μμ. They represented their results by the formula $\mu-1=5{\cdot}6685\times10^{27}(11416\times10^{27}-\lambda^2)^{-1}$. M. Faraday said that the liquid refracts light less than all other liquids he tried. L. Bleekrode gave for the refractive index of the gas 1·000503, and 1·204 for the liquid. He also gave $(\mu-1)/D$=0·255 for the gas, and 0·235 for the liquid; while $(\mu^2-1)/(\mu^2+2)D$=0·170 for the gas, and 0·150 for the liquid. W. Herz studied the refraction of nitrous oxide. J. Koch measured the **dispersion.** H. Becquerel gave for the **magnetic rotation** of the plane of polarization of the gas with Na-light, 16·02, or 0·00393 with that of liquid carbon disulphide. C. E. Guye and R. Rudy studied the electromagnetic rotation of nitrous oxide. C. V. Raman and K. S. Krishnan gave $0{\cdot}48\times10^{-10}$ for Kerr's constant at 20°. Lord Rayleigh, and J. Cabannes and J. Granier studied the polarization of light laterally diffused in nitrous oxide. F. Holweck studied the absorption spectrum. A. Dufour found that in the neighbourhood of the bands $\lambda=585{\cdot}49\mu\mu$ and 584·68, the ordinary effect is produced, but with the bands $\lambda=592{\cdot}54\mu\mu$ and $585{\cdot}69\mu\mu$, the inverse effect is obtained. W. H. Bair, and H. O. Kneser studied the **spectrum** of nitrous oxide; and S. W. Leifson, the ultra-violet absorption spectrum. M. F. Skinker and J. V. White investigated the motion of electrons in nitrous oxide.

M. A. Hunter[13] showed that platinum electrodes are not polarized by nitrous oxide, and he estimated that the **oxidation potential** of nitrous oxide is about 0·39 volt higher than that of oxygen. G. Gehlhoff studied the cathode fall of potential during an electric discharge in a vacuum tube; E. P. Metcalfe, the ionization of the gas; L. B. Loeb, and M. F. Skinker and J. V. White, the mobilities of ions in the gas; W. G. Palmer, the effect of nitrous oxide on the coherer in detecting electric waves. F. M. Bishop found the ionizing potential to be the same as that of nitrogen. The **dielectric constant** of nitrous oxide gas was found by L. Boltzmann[14] to be 1·000497, and by J. Clemencic, 1·000579. F. Linde found the dielectric constant of liquid nitrous oxide to be 1·643 at −6°; 1·591 at −0·5°; 1·582 at 4°; 1·55 at 10°; and 1·522 at 14·5°; and for nitrous oxide gas at 15°, 1·070 at 39 atm. press.; 1·051 at 29·8 atm.; 1·026 at 19·9 atm.; and 1·010 at 9·4 atm. W. Herz studied some relations between the dielectric constant and the physical properties. G. Quincke obtained $+0{\cdot}12\times10^{-6}$ mass units for the **magnetic susceptibility** of nitrous oxide, at 16° and 40 atm. press.; T. Soné said that nitrous oxide is diamagnetic with the sp. susceptibility $-0{\cdot}43\times10^{-6}$, and this constant has the same value whether the compound is liquid or gaseous. The subject was studied by N. W. Taylor and G. N. Lewis, and A. E. Oxley.

The solubility of nitrous oxide in different solvents.—H. Davy[15] said that at ordinary temp. one vol. of *water* dissolves 0·54 vol. of the gas, and J. Priestley said that the dissolved gas is driven unchanged from the boiling liquid. The solubilities measured by N. T. de Saussure, W. Henry, J. Dalton, and A. M. Pleischl ranged from 0·708 to 0·80. These numbers are not discordant with later values obtained at specified temp. by W. Knopp, V. Gordon, G. Geffcken, W. Roth, etc. R. Bunsen gave for the coeff. of absorption, β, and G. Geffcken for the solubility, S, expressed as a ratio of the vol. of gas absorbed at θ° to the vol. of the absorbing liquid:

	5°	10°	15°	20°	25°
β . . .	1·0950	0·9196	0·7778	0·6700	0·5961
S . . .	1·067	0·9101	0·7784	0·6756	0·5992

L. Carius, and G. Wiedemann represented their results at θ° by $\beta=1{\cdot}30521-0{\cdot}0453620\theta+0{\cdot}00068430\theta^2$; and M. Bellati and S. Lussana, $\beta=1{\cdot}30224-0{\cdot}046184\theta+0{\cdot}0007190 4\theta^2$. The effect of press. on the solubility was found by A. Findlay and O. R. Howell to be independent of press. within 758 and 1362 mm. in that the ratio of the conc. of the gas in the gaseous and solution phases remained constant at 0·592. Liquid nitrous oxide is not completely miscible with water. As shown by M. Faraday, and T. Wills, there is formed a soln. of nitrous oxide in water on which floats what is probably a soln. of water in liquid nitrous oxide. M. L. Nichols and I. A. Derbigny stated that nitrous oxide forms with water a soln. having acidic properties: $N_2O+H_2O=(NOH)_2$. According to P. Villard, water forms with nitrous oxide a crystalline **hexahydrated nitrous oxide,** $N_2O.6H_2O$. It is produced by keeping a mixture of liquid nitrous oxide and water in the presence of mercury in a sealed tube standing for some time in ice. The tube, at 0°, is opened and the gas allowed to escape. The acicular, or tabular crystals are said to belong to the cubic system; to have a sp. gr. 1·15; to be stable below 0° at atm. press.; and to have a heat of formation $(N_2O,6H_2O)=15$ Cals. G. Tammann and G. J. R. Krige found the dissociation press., p, at the temp. θ to be $\theta=19{\cdot}4\ (\log p-0{\cdot}9795)$.

G. Lunge measured the solubility of the oxide in sulphuric acid and found that 100 vols. of acid of sp. gr. 1·84 dissolved 75·7 vols. nitrous oxide; sp. gr. 1·80, 66·0 vols.; sp. gr. 1·705, 39·1 vols.; sp. gr. 1·45, 41·6 vols.; and sp. gr. 1·25, 33·0 vols.

G. Geffcken obtained the following results for the solubility, S, in *hydrochloric, nitric, and sulphuric acids;* and W. Roth, for the coeff. of absorption, β, for *phosphoric and oxalic acids:*

		5°	15°	25°
S, HCl	18·22 per cent.	—	0·755	0·577
	72·90 ,,	—	0·716	0·557
S, HNO_3	36·52 ,,	—	0·777	0·597
	126·10 ,,	—	0·775	0·611
S, H_2SO_4	24·52 ,,	—	0·734	0·566
	98·08 ,,	—	0·645	0·509
	196·16 ,,	—	0·662	0·463
β, H_3PO_4	3·38 ,,	1·0570	0·7388	0·5427
	13·35 ,,	0·9171	0·6505	0·4860
β, $H_2C_2O_4$	0·812 ,,	1·1450	0·7940	0·5784
	3·70 ,,	1·1094	0·7745	0·5643

W. Manchot found that the results with sulphuric, nitric, and hydrochloric acid soln. differ from those with salts, for, with rising concentration, the solubility first falls, reaches a minimum, and then increases—Fig. 67. W. Knopp found that at 20° aq. soln. containing 15·15, 158·4, and 344·0 grms. of *propionic acid* per litre have the coeff. of absorption: 0·6323, 0·6504, and 0·7219 respectively. Using S for the solubility as indicated above, and β for the coeff. of absorption, G. Geffcken found for soln. with 53·52 grms. of *ammonium chloride* per litre, $S=0·691$ at 15°, and $S=0·529$ at 25°; and with 42·48 grms. of *lithium chloride,* $S=0·623$ at 15°, and 0·483 at 25°. Observations with lithium chloride were also made by V. Gordon, who found for soln. with 12·78 grms. of *sodium chloride* per litre, $\beta=0·634$ at 5°, and 0·386 at 20°. W. Roth made more detailed observations with this salt. G. Geffcken gave for the soln. with 74·6 grms. of *potassium chloride* per litre, $S=0·616$ at 15°, and 0·475 at 25°. Observations with potassium chloride were also made by V. Gordon, and N. T. de Saussure. G. Geffcken also found for soln. with 120·95 grms. of *rubidium chloride* per litre, $S=0·625$ at 15°, and 0·483 at 25°; for soln. with 84·17 grms. of *cæsium chloride* per litre, $S=0·710$ at 15°, and 0·544 at 25°. V. Gordon found for soln. with 13·99 grms. of *calcium chloride* per litre, $\beta=0·510$ at 5°, and 0·328 at 20°; and for soln. with 13·24 grms. of *strontium chloride* per litre, $\beta=0·644$ at 5°, and 0·391 at 20°. G. Geffcken gave for soln. with 119·11 grms. of *potassium bromide* per litre, $S=0·627$ at 15°, and 0·485 at 25°; for soln. with 166·12 grms. of *potassium iodide* per litre, $S=0·633$ at 15°, and 0·492 at 25°. V. Gordon gave for soln. with 8·56 grms. of *lithium sulphate* per litre, $\beta=0·646$ at 5°, and 0·415 at 20°; for soln. with 12·44 grms. of *sodium sulphate* per litre, $\beta=0·559$ at 5°, and 0·354 at 20°; for soln. with 4·78 grms. of *potassium sulphate* per litre, $\beta=0·918$ at 5°, and 0·542 at 20°; and for soln. with 10·78 grms. of *magnesium sulphate* per litre, $\beta=0·569$ at 5°, and 0·346 at 20°. G. Geffcken found that 100 vols. of conc. soln. of *ferrous sulphate* absorb 19·5 vols. of nitrous oxide. W. Knopp gave for soln. with 11·37 and 95·30 grms. of *sodium nitrate* per litre, at 20°, respectively $\beta=0·6089$ and 0·4926; and for soln. with 10·74 and 118·2 grms. of *potassium nitrate* per litre at 20°, respectively $\beta=0·6173$ and 0·5196. G. Lunge found that 100 vols. of a soln. of *sodium hydroxide,* sp. gr. 1·10, absorb 23·1 vols. of nitrous oxide; and 100 vols. of a soln. of *potassium hydroxide,* sp. gr. 1·12, absorb 18·7 vols. of nitrous oxide. G. Geffcken gave for soln. with 28·08 and 56·16 grms. of potassium hydroxide per litre, $S=0·668$ and 0·559 respectively at 15°; and 0·514 and 0·436 at 25°; with 100 vols. of sodium hydroxide sat. with *pyrogallol,* 28 vols. of nitrous oxide were absorbed. W. Manchot's results with soln. of the chlorides of ammonium, potassium, sodium, calcium, and barium; bromides of ammonium, potassium, and sodium; nitrates of ammonium, potassium, sodium, copper, calcium, magnesium, zinc, cadmium, and aluminium; sulphates of ammonium, potassium, sodium, magnesium, zinc, aluminium, manganese, iron (ous and ic), cobalt, nickel, and chromium; sodium hydrophosphate, sodium orthophosphate, and potassium periodate, are illustrated in Fig. 67.

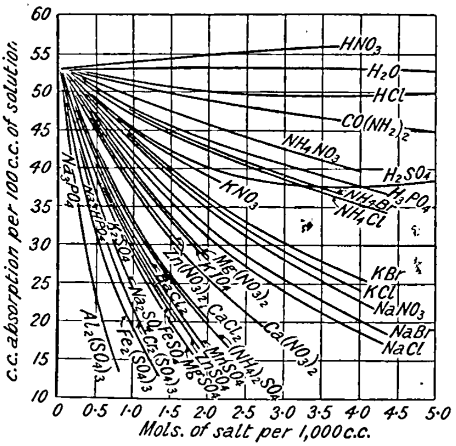


FIG. 67.—The Solubility of Nitrous Oxide in Salt Solutions.

W. Manchot calculated the results to show the effect of equal weights of water in the soln., and he attempted to calculate the number of mols of water required by the various ions.

A. Findlay and co-workers measured the effect of press. on the solubility of nitrous oxide on colloidal soln. of *ferric hydroxide* of different conc. Thus, with 0·625, 1·49, and 4·061 grms. of ferric hydroxide per 100 c.c. of soln., the solubility of nitrous oxide is respectively 0·590, 0·586, and 0·578 at press. approximating 750 mm., 0·584, 0·577, and 0·571 at press. approximating 930 mm., and 0·588, 0·586, and 0·580 at press. approximating 1350 mm. The solubility in colloidal soln. of *arsenious sulphide* is similar; G. Geffcken also measured this effect with ferric hydroxide and arsenious sulphide. A. Findlay and H. J. M. Creighton found that the solubility in silicic acid increases with increasing conc. of *silicic acid*, and with increasing press.

H. Davy found nitrous oxide is soluble in *alcohol* and *ether*; and N. T. de Saussure said that 100 vols. of alcohol of sp. gr. 0·840 absorb 153 vols. of gas. R. Bunsen gave for the solubility of nitrous oxide in alcohol, expressed in vols. of gas, reduced to 0° and 760 mm., per vol. of alcohol:

	0°	5°	10°	15°	20°	24°
N_2O . .	4·178	3·844	3·541	3·268	3·025	2·853

L. Carius found the absorption coeff. of nitrous oxide in alcohol at 760 mm. press. at $\theta°$ to be $\beta=4{\cdot}17805-0{\cdot}0698160\theta+0{\cdot}0006090\theta^2$; and M. Bellati and S. Lussana, $\beta=4{\cdot}19044-0{\cdot}074477\theta+0{\cdot}0007857\theta^2$. G. Lunge's proposal to determine the gas by absorption with absolute alcohol is, according to L. W. Winkler, too inexact. W. Kunerth found the solubility of nitrous oxide at 20° in water, 0·675; in *methyl alcohol*, 3·32; in ethyl alcohol, 2·99; in *isoamyl alcohol*, 2·47; in *acetone*, 6·03; in *acetic acid*, 4·85; in *pyridine*, 3·58; in *chloroform*, 5·60; in *benzaldehyde*, 3·15; in *aniline*, 1·48; in *amyl acetate*, 5·14; and in ethylene bromide, 2·81 c.c. of gas at the prevailing press. per c.c. of solvent. W. Knopp found the coeff. of absorption of nitrous oxide in soln. with 30·43 and 316·4 grms. of *chloral hydrate* per litre at 20° to be respectively 0·618 and 0·567. W. Roth found for soln. with 3·46 and 16·24 per cent. of *glycerol* $\beta=1{\cdot}097$ and 0·959 respectively at 5°; and 0·556 and 0·508 respectively at 25°; likewise for soln. with 3·31 and 9·97 per cent. of *urea*, $\beta=1{\cdot}104$ and 1·069 respectively at 5°, and 0·569 in both cases at 25°. S. H. Steiner found that the coeff. of absorption of soln. with 1·699 and 0·520 mols of *cane-sugar* per litre at 15° is 0·0892 and 0·1561 respectively. A. Findlay and co-workers found with increasing conc. of *dextrin*, the solubility fell from 0·549 with 6·98 grms. of dextrin per 100 c.c. to 0·503 with 20·30 grms. The solubility increased with increasing press. Analogous results were obtained with *starch*, *gelatin*, and *glycogen*; while with *egg-albumen*, and *serum-albumen* the solubility curves give a minimum with increasing press. being 0·583, 0·579, and 0·591 respectively at 746, 978, and 395 atm. press. for a soln. with 0·32 grm. of *serum-albumen* per 100 c.c. Hence, the solubility with these colloidal soln. no longer follows Henry's law. This may be due to a polymerization of the gas or to adsorption effects. R. Siebeck, and A. Findlay and co-workers measured the solubility of nitrous oxide in *blood*. The first-named observed that the absorption coeff. of water for nitrous oxide is smaller than that of blood. The increased absorption is not due to the plasma, the coeff. of which is 97·5 per cent. of that of water. On the other hand, a soln. of red corpuscles has a markedly greater coeff. than water, and the absorption in this soln. obeys Henry's law, and is independent of the absorption of carbon dioxide and oxygen. Nitrous oxide is soluble in *fixed and volatile oils*. N. T. de Saussure found that 100 vols. of rectified *naphtha* of sp. gr. 0·784 absorb 254 vols. of gas; 100 vols. of *turpentine*, 250–270 vols. of gas; 100 vols. of *oil of lavender* of sp. gr. 0·880 absorb 275 vols.; and 100 vols. of *olive oil* of sp. gr. 0·915, 150 vols. of gas. S. Gniewasz and A. Walfisz found for *petroleum*, at 10°, $\theta=2{\cdot}49$, and at 20°, 2·11.

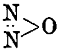
According to P. A. Favre, one c.c. of *charcoal* absorbs 99 c.c. of nitrous oxide; and, according to N. T. de Saussure, 40 c.c. The heat of absorption is 3718 cals. per equivalent. A. Findlay and H. J. M. Creighton found that with charcoal suspended in water and nitrous oxide,

Pressure	950	1000	1050	1150	1250	1350
Gas absorbed by solid C_1 . .	0·0059	0·0085	0·0109	0·0151	0·0200	0·02
Gas dissolved by water, C_2 .	0·1332	0·1402	0·1472	0·1613	0·1753	0·18
C_1/C_2	0·058	0·048	0·043	0·045	0·047	0·05

L. B. Richardson and J. C. Woodhouse studied the absorption of mixtures of carbon dioxide and nitrous oxide by charcoal; S. J. Gregg, the heat of adsorption; D. H. Bangham and F. P. Burt, the adsorption of nitrous oxide by *glass*; and W. A. Patrick and co-workers, by *silica gel* near the critical temp. of the gas.

The chemical properties of nitrous oxide.—Nitrous oxide was analyzed by

H. Davy,[16] J. L. Gay Lussac and L. J. Thénard, and J. R. Deiman and co-workers. The results of H. Davy are in harmony with the empirical formula N_2O. This also agrees with analyses by A. Jaquerod and S. Bogdan, and E. H. Keiser. The density of the gas is in agreement with the simplest formula. The mol. is generally supposed to have two tervalent nitrogen atoms, and to be constituted:


$$\begin{matrix} N \\ \vdots \\ N \end{matrix} > O$$

—not N.O.N by analogy with H.O.H. There are other possibilities, *e.g.* W. A. Noyes favoured, but W. T. Hall objected to the formula $O{=}N{\equiv}N$ recommended by H. Henstock. G. Kirsch, A. E. Oxley, J. R. Partington, A. O. Rankine, C. D. Niven, and A. W. C. Menzies discussed the at. and mol. structure. According to K. A. Hofmann, and L. Pauling and S. B. Hendricks, the chemical evidence favours the constitution $N{\equiv}N{=}O$, rather than $N_2{>}O$. J. C. Thomlinson tried to calculate the eq. of nitrogen in nitrous oxide from thermochemical data; and he considered that the results agree with the assumption that nitrous oxide contains quinquevalent nitrogen; G. le Bas said that the mol. vol. agrees with the 3-membered ring formula


$$\begin{matrix} \cdot{<}N \\ \vdots \\ \cdot{<}N \end{matrix} > O$$

A. O. Rankine found that the mols. of nitrous oxide and carbon dioxide behave physically as if they had the same size, shape, and electronic structure. I. Langmuir compared the physical properties of carbon dioxide and of nitrous oxide, and the similarity was attributed to a like electronic structure—*vide* **4.** 27, 4, Fig. 30. G. Kirsch made observations on the electronic structure of the molecule; and M. L. Huggins made estimates of the interatomic distances.

Nitrous oxide, or a gas with an analogous composition, is the anhydride of hyponitrous acid, $H_2N_2O_2$, and could be called **hyponitrous anhydride.** Owing to our defective notation, it cannot be called nitrous anhydride by analogy with the nomenclature employed in many other cases. Nitrous anhydride, N_2O_3, is the anhydride of nitrous acid, HNO_2. To adjust the nomenclature, nitrous oxide would have to be called **hyponitrous oxide.** While the action of water on nitrous or hyponitrous anhydride does not form hyponitrous acid, yet the dehydration of hyponitrous acid by conc. sulphuric acid forms nitrous or hyponitrous oxide: $H_2SO_4+H_2N_2O_2=H_2SO_4.H_2O+N_2O$.

J. Priestley [17] showed that nitrous oxide is decomposed into its elements when passed through a red-hot porcelain tube, and at the same time a higher oxide is formed. M. Berthelot found that after heating for half an hour at 520°, about 1·5 per cent. of the gas is decomposed, and at the same time, some of the higher oxides are formed. C. Langer and V. Meyer observed that the decomposition is complete at 900°. According to G. T. Kemp, C. Winkler's proposal to estimate the nitrous oxide in some gaseous mixtures by decomposing this gas: $2N_2O=2N_2+O$ by passing it over red-hot palladium, is inexact. M. A. Hunter found that the course of the decomposition at 713°, 805°, and 895° corresponds with that of a bimolecular reaction; and the influence of temp. on the velocity constant, k, is represented by $\log k=31800T+24{\cdot}12$. The influence of moisture on the reaction is not appreciable. S. Dushman studied these results. L. Maquenne found that when a small quantity of mercury fulminate is exploded in contact with nitrous oxide, the latter is decomposed. According to E. Briner and A. Wroczynsky, nitrous oxide is more stable than nitric oxide in that it requires a higher temp. to show an appreciable decomposition. At 600 atm. and 420°, it suffers a slight decomposition. According to C. N. Hinshelwood and co-workers, the heterogeneous thermal decomposition of nitrous oxide on the surface of a heated platinum wire between 600° and 1200° is retarded by the presence of oxygen and proceeds at a relatively faster rate at low than at high press.

The velocity of the reaction is represented by the equation $-d[N_2O]/dt = k[N_2O]/(1+b[O_2])$, and the heat of activation in the catalytic reaction is 32,500 cals. per mol. This reaction is unimolecular, whereas the homogeneous thermal decomposition of nitrous oxide is bimolecular and its heat of activation is much greater; the platinum surface in the heterogeneous reaction acts as an acceptor for atomic oxygen, the nitrous oxide probably giving its oxygen atom to the platinum, thereby forming a retarding film of at. oxygen. They also studied the decomposition of nitrous oxide on the surface of heated gold and found the unimolecular process is a true wall-reaction. S. Uchida found that the reaction is of the first order, and that the velocity constant of the decomposition of nitric oxide is 0·39 with platinum gauze as catalyst, and 0·013 with ferric oxide as catalyst at a temp. of 600°. R. C. Tolman studied the different ways of activating the molecules in the bimolecular reaction $2N_2O=2N_2+O_2$. E. Briner and co-workers observed that when nitrous oxide is circulated through a heated fused silica tube, at 1300°, 25 per cent. of the gas is converted into nitric oxide, and the amount is lowered by the presence of powdered quartz or platinum. It is suggested that the nitrous oxide breaks down simultaneously in two ways, $N_2O \rightarrow N_2+\frac{1}{2}O_2+20{\cdot}6$ Cals., and $N_2O \rightarrow NO+\frac{1}{2}N_2-0{\cdot}9$ Cal. The reaction was studied by C. Meiner, F. A. Constable, and E. J. Bowen. J. Priestley found that the gas is decomposed by long-continued sparking; and W. R. Grove added that at the same time there is an increase in volume from 1 to 1·5; with a more protracted action, red fumes of the higher oxides appear. These results were confirmed by H. Buff and A. W. Hofmann, and M. Berthelot. S. S. Joshi studied the decomposition of nitrous oxide by the silent electrical discharge in the press. range 110–820 mm. The end-products are nitrogen and oxygen, but the intermediate products indicate that the reaction actually involves two simultaneous reactions: $2N_2O=2NO+N_2$ and $2N_2O=2N_2+O_2$, followed by $2NO+O_2=2NO_2$, or else it involves the three consecutive reactions: $4N_2O=4NO+2N_2$; $2NO=N_2+O_2$; and $2NO+O_2=2NO_2$. The time required for total decomposition increases rapidly with increase of gas press., and the mean rate of decomposition increases with an increase in the potential applied to the reaction vessel, and diminishes as the gas press. increases. A. Geitz studied the dissociation of nitrous oxide by the high-tension arc-flame; and E. Wourtzel, by a stream of α-rays from radium: $N_2O=NO+N$. D. Berthelot and H. Gaudechon observed that nitrous oxide is partly decomposed into its elements when exposed to the light from a mercury quartz lamp, and the oxygen so formed unites with the undecomposed gas to form higher oxides. E. Warburg and E. Regener found that nitrous oxide is decomposed by radiations of short wave-length from a spark discharge. The wave-length of the active ray is under $0{\cdot}3\mu$.

In his early work on this gas, J. Priestley[18] noticed that nitrous oxide is not combustible; a candle will burn in the gas more brilliantly than in air; a glowing splint, when immersed in the gas, bursts into flame. J. Priestley said:

> Sometimes I have perceived the flame of a candle in the circumstances to be twice as large as it is naturally, and sometimes not less than five or six times larger; and yet without anything like an explosion, as in the firing of the weakest inflammable air. . . . At the time of my first publication on this subject, I should not have hesitated to pronounce as impossible (that) air in which a candle burns naturally and freely, (would be) in the highest degree noxious to animals, insomuch that they die the moment they are put in it.

H. B. Dixon and W. F. Higgins found that when the air feeding the flame of **hydrogen,** methane, ethylene, or propylene is replaced by nitrous oxide, there is a pretty transformation scene. It is possible to read by the hydrogen flame in nitrous oxide although the flame is almost invisible in air. Fig. 68 illustrates the great contrast between the two flames. The hydrocarbons give a core of white light with an apricot-coloured, and then a large, greenish-grey sheath. The flames are magnified roughly five times in height and twice in diameter. No peroxide could be detected in the interconal gases, but it is found in the gases of the outer flame.

The ignition points, $\theta°$, of hydrogen, ethylene, and propylene in nitrous oxide, with a 0·5 sec. lag, at different press., p mm., are :

	p	1000	760	550	400	250	150	100
θ	H_2	594°	597°	572°	549°	524°	504°	—
	C_2H_4	—	592°	605°	605°	592°	578°	570°
	C_3H_6	—	586°	605°	623°	620°	608°	—

All these gases ignite in nitrous oxide at a lower temp. than they do in air. J. Priestley, H. Davy, and W. Henry observed that if nitrous oxide be mixed with hydrogen in equal vols., and ignited by an electric spark, or a red-hot tube, the detonation is attended by the formation of water and nitrogen: $N_2O+H_2=N_2+H_2O$; if less hydrogen be used, some nitric acid is produced ; the reaction is utilized in gas analysis. G. T. Kemp, and G. Lunge obtained high results, but O. von Dumreicher, L. H. Milligan, and W. Hempel obtained satisfactory results when an excess of hydrogen is used—say 2 or 3 times the vol. of that of the nitrous oxide.

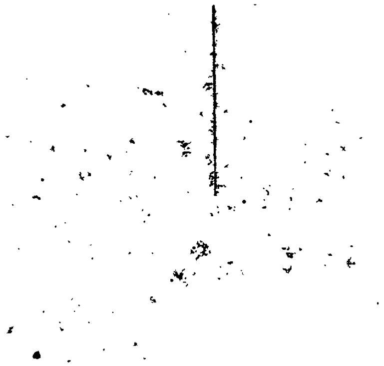


FIG. 68.—Flames of Hydrogen in Nitrous Oxide and in Air.

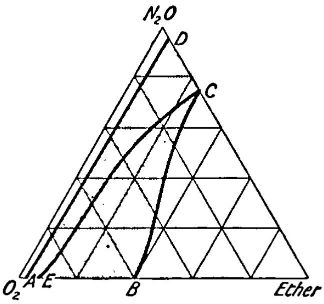


FIG. 69.—Explosive Limits with $N_2O-(C_2H_5)_2O-O_2$ (and Air).

W. K. Hutchison and C. N. Hinshelwood measured the rate of the reaction $N_2O+H_2=N_2+H_2O$ (liquid) on the surface of gold wire at 704° and 880°. Both gases are adsorbed independently by the gold, and the rate of the reaction tends to a limiting value as the press. of each gas is increased showing that the surface of the gold approaches a state of saturation. With hydrogen, there is a complication due to the absorption of hydrogen as distinct from adsorption. H. B. Dixon found the velocity of explosion of mixtures of nitrous oxide and hydrogen, $H_2+N_2O=H_2O+H_2$, to be 2305 metres per second ; and M. Berthelot and P. Vieille, 2284 metres per second. According to W. P. Jorissen and B. L. Ongkiehong, the explosive regions with mixtures $N_2O—(C_2H_5)_2O—O_2$ can be represented by the regions *ABCD*, Fig. 69 ; and with mixtures $N_2O—(C_2H_5)_2O$—air, by the region *ADCE*. On adding air to the mixture with oxygen, the line *CB*, revolving about *C*, moves to the left, and finally coincides with *CE*. If the ignition spark is strong enough to start a reaction with $H_2O—O$ mixture, which propagates itself, the line *AD* will revolve about *A* and cut the left side of the triangle. C. Winkler recommended estimating the nitrous oxide in some gaseous mixtures by adding an excess of hydrogen, and passing the mixture over heated platinized asbestos: $N_2O+H_2=H_2O+N_2$. L. Duparc and co-workers found that while hydrogen in the presence of metals of the platinum group reduces nitric oxide to ammonia, nitrous oxide is reduced to nitrogen. H. S. Taylor and A. L. Marshall studied the reduction of the gas by the activated hydrogen. The reduction of nitrous oxide to ammonia by hydrogen in the presence of platinum sponge or platinum or palladium black has been studied by J. W. Döbereiner, P. L. Dulong and L. J. Thènard, F. Kuhlmann, M. A. Hunter, C. N. Hinshelwood, H. S. Taylor,

C. Montemartini, etc.—*vide* ammonia; and in the presence of nickel and copper, by P. Sabatier and J. B. Senderens. According to P. A. Guye and F. Schneider, nitrous oxide is reduced by nickel and hydrogen much more slowly than is the case with nitric oxide. No nitrous oxide is formed during the reduction of nitric oxide by nickel and hydrogen, but it may be formed when nitric oxide is reduced by sulphur dioxide. M. Berthelot could not detect the formation of a higher oxide when a mixture of **oxygen** and nitrous oxide is heated to dull redness. M. Berthelot and H. Gaudechon found that a mixture of nitrous oxide and oxygen forms higher nitrogen oxides when exposed to ultra-violet light. For the action of water, *vide supra*. The gas, and an aq. soln. of the gas, has no action on vegetable colours—litmus, etc.

H. Moissan and P. Lebeau found that **fluorine** does not react with nitrous oxide at a dull red heat. If a mixture of the two gases be heated electrically by means of a platinum spiral, platinum fluoride is formed at 400°, or if the two gases are heated to redness in a glass vessel, silicon fluoride and oxygen are formed, whilst the nitrous oxide remains unaltered. When a mixture of nitrous oxide and fluorine is submitted to the action of an induction spark in the presence of mercury, there is a complex reaction, the mercury is attacked, and the final gaseous mixture contains oxygen, nitrogen, and nitrous oxide, but no compound of nitrogen and fluorine. A. J. Balard did not detect any reaction between nitrous oxide and **chlorine monoxide** in the cold. J. B. A. Dumas observed no reaction between **iodine** and liquid nitrous oxide. O. von Dumreicher observed that nitrous oxide forms a white cloud when treated with **hydrogen iodide,** the cloud gradually reddens, and crystals of iodine appear: $N_2O+10HI=2NH_4I+H_2O+4I_2$. K. A. Hofmann and co-workers said that probably on account of its saturated nature, nitrous oxide does not react with potassium chloride at 360°, and it is also very sluggish in its action towards hydrogen and carbon monoxide in contrast with the vigorous action of potassium chlorate and ammonia.

H. Davy found that feebly burning **sulphur** continues burning vigorously in the gas, with a bright greenish-blue flame; sulphur dioxide is formed, and one vol. of nitrous oxide gives one vol. of nitrogen. According to A. Stavenhagen and E. Schuchard, if the combustion of sulphur in nitrous oxide be carried out in a large glass vessel, the walls become covered with crystals of nitrosulphonic acid, and, at the same time, nitrogen peroxide is formed in quantity. Thus, nitrous oxide may be transformed into higher oxides of nitrogen without the use of electrical energy by simply burning sulphur in it, nitrosulphonic acid anhydride or its decomposition products being formed at the same time. J. B. A. Dumas observed no reaction between liquid nitrous oxide and sulphur. G. Chevrier, and M. Berthelot observed that a mixture of sulphur vapour and nitrous oxide is inflamed by an electric spark, forming sulphur dioxide and nitrosopyrosulphuric anhydride. A mixture of **hydrogen sulphide** and nitrous oxide, with an electric spark or at a red-heat, furnishes sulphur dioxide, water, and nitrogen. P. Pascal said that a high conc. of **sulphur dioxide** reduces nitrous oxide to nitrogen if the temp. be high. E. J. B. Willey and E. K. Rideal found that nitrous oxide is not decomposed by active **nitrogen.** A mixture of nitrous oxide and **ammonia** is reduced by an electric spark, or when heated to redness, forming nitrogen and water. A. Joannis found that when nitrous oxide is passed into a soln. of potassium or sodium in liquid ammonia, an amide is formed: $N_2O+2KNH_3=KNH_2+NH_3+KOH+N_2$, and with a more protracted action, a nitride is produced: $2KNH_2+N_2O=KN_3+KOH+NH_3$. Unlike oxygen, when nitrous oxide is mixed with a little **nitric oxide,** it does not produce red fumes, nor suffer a diminution in vol. J. R. Deiman and co-workers observed that fuming **nitric acid** reduces the vol. of nitrous oxide, and P. T. Austen, that moist nitrous oxide reacts with the vapour of nitric acid, forming ammonium nitrate. F. Raschig observed that **nitrous acid** reacts with nitrous oxide, forming nitric oxide. H. B. Dixon and J. D. Peterkin observed a slight expansion on mixing nitrous oxide and **nitrogen peroxide,** thus indicating a slight dissociation of the N_2O_4-mols. H. Davy found that **phosphorus** can be volatilized, or touched with a red-hot iron rod in an atm. of nitrous oxide without inflammation; but if a white-hot iron rod is used, or if the phosphorus be vigorously burning when immersed in the gas, it burns as brilliantly as in oxygen, forming phosphorus pentoxide, and some nitrogen peroxide. J. B. A. Dumas observed no reaction with liquid nitrous oxide and phosphorus. According to P. Thénard, spontaneously inflammable **phosphine** detonates with nitrous oxide at ordinary temp. The reaction was studied by J. J. Berzelius, T. Thomson, and J. B. A. Dumas; it is symbolized by $2PH_3+8N_2O=P_2O_5+3H_2O+8N_2$ (or $2H_3PO_4+8N_2$).

H. Davy found that glowing **carbon** burns as vigorously in nitrous oxide as in oxygen: $2N_2O+C=CO_2+2N_2$; but J. B. A. Dumas observed no reaction between liquid nitrous oxide and carbon, but a glowing piece of charcoal swims on the liquid while burning vigorously. H. Davy found that a mixture of **carbon monoxide** and nitrous oxide can be detonated by electric sparks; and that the same result occurs with a mixture of nitrous oxide and **cyanogen,** or of nitrous oxide and a **hydrocarbon.** W. Henry referred to the vivid combustion of a mixture of nitrous oxide and olefiant gas; and H. B. Dixon and W. F. Higgins' observations have been previously described. W. Henry, and G. T. Kemp recommended determining the nitrous oxide in some gaseous mixtures by adding about 7 vols. of carbon monoxide to one vol. of nitrous oxide, $CO+N_2O=CO_2+N_2$, and estimating the resulting carbon dioxide by absorption with alkali-lye. If the gases are moist there is a disturbing side reaction: $CO+H_2O=CO_2+H_2$. M. Berthelot and P. Vieille gave for the velocity of the explosion: $CO+N_2O=CO_2+N_2$, 1106 metres per second. J. B. A. Dumas found that a mixture of liquid nitrous oxide and **carbon disulphide,** or **alcohol,** or **ether** will freeze mercury, sulphuric acid, or nitric acid; and J. O. Natterer said that in vacuo a temp. of −140° can be obtained with a mixture of liquid nitrous oxide and carbon disulphide—*vide supra* for the combustion of ether in the gas. Heated **boron** burns in the gas, forming, according to H. Davy, boric oxide, and, according to H. St. C. Deville and F. Wöhler, some boron nitride.

J. L. Gay Lussac and L. J. Thénard found that when **sodium** or **potassium** is heated in the gas, the combustion is vigorous, forming alkali peroxide, and nitrite, as well as oxygen and nitrogen. P. Sabatier and J. B. Senderens found that **copper** above 150° is slowly transformed into cuprous oxide. E. Schröder and G. Tammann measured the rate of oxidation of copper by nitrous oxide. P. Sabatier and J. B. Senderens found that **magnesium** powder in contact with water and nitrous oxide reacts with the evolution of much hydrogen; **zinc** filings act similarly —hydrogen and nitrogen are produced together with some ammonia. H. Davy found that zinc is slowly oxidized at a red-heat. P. Sabatier and J. B. Senderens observed that **cadmium** is gradually oxidized by the gas at 300°. H. Davy found that **manganese** and **tin** are oxidized by the gas at a red-heat; and P. Sabatier and J. B. Senderens observed that **lead** is oxidized at 300°; **iron** burns in the gas below 170°, forming ferric oxide; and at ordinary temp., in the presence of moisture, nitrous oxide is reduced to nitrogen and some hydrogen is produced. J. Priestley said that iron filings burn in nitrous oxide as vigorously as in oxygen. E. Schröder and G. Tammann measured the rate of oxidation of iron and **nickel** by nitrous oxide. P. Sabatier and J. B. Senderens observed that **cobalt** burns in nitrous oxide at 230°, forming cobaltous oxide; nickel likewise forms green nickelous oxide; and **palladium hydride** at 250° produces water; while **palladium** itself is not changed. E. Schröder and G. Tammann compared the rates of oxidation of metal by oxygen, nitric oxide, and nitrous oxide.

J. Persoz said that nitrous oxide reacts with moist **potassium hydroxide,** forming nitric acid and ammonia, or ammonium nitrate, but later considered that these substances were derived from some ammonium nitrate mechanically mixed with the gas prepared from that salt. M. Berthelot could find no trace of ammonia when the nitrous oxide is passed over red-hot **soda-lime**; alcoholic potash at 100°–200°; or potash-lye at 300°. P. Sabatier and J. B. Senderens found that at 200°, nitrous oxide reacts with **sodium dioxide,** forming sodium nitrite and nitrogen; and with **barium dioxide** in an analogous manner at 500°–600°; **manganous oxide** at 350° forms Mn_3O_4 with inflammation; **tungsten dioxide** at 450° forms the blue oxide; **molybdenum monoxide** below 500° forms the violet oxide; **stannous oxide** at 400° forms stannic oxide; **cuprous oxide** at 350° is not changed; **lead dioxide** at 200° forms litharge and oxygen; **uranium dioxide** at 450° is not changed. V. Kohlschütter and K. Vogdt, and C. Friedheim discussed solid soln. of nitrous oxide and **uranium trioxide.** A. Wagner found that when nitrous oxide is passed over a heated mixture of **chromic oxide** and sodium carbonate, sodium chromate is produced. He recommended the reaction as a means of estimating nitrous oxide in some gaseous mixtures since nitric oxide does not react in this way. As a rule, nitrous oxide is fairly stable towards **oxidizing agents**; an alkaline soln. of **potassium permanganate** was found by J. A. Wanklyn and W. J. Cooper to be unaffected by nitrous oxide at 100°; and O. von Dumreicher observed that **stannous chloride** does not reduce nitrous oxide. Similarly, **stannous salts, alkali sulphides or sulphites,** and **ferrous salts** have no action on nitrous oxide; nor is the gas dissolved by soln. of ferrous salts—*confer* nitric oxide and soln. of ferrous salts. M. Coblens and J. K. Bernstein found that **titanous chloride** reduces nitrous oxide to ammonia. M. L. Nichols and I. A. Derbigny showed that in the reduction of nitrous oxide by stannous chloride, titanous chloride, and sodium sulphite, at 25°, ammonia, hydroxylamine, and nitrogen are respectively formed. The rate of reduction increases with increasing conc. of the reducing agent, decreases with a rise in temp., and, in the case of stannous chloride and titanous chloride, decreases with increased (hydrochloric) acid conc. The reduction of nitrous oxide by titanous chloride is catalyzed by platinum. The mechanism of the reduction is thought to depend on the initial formation of hyponitrous acid, according to the equation $N_2O+H_2O=(NOH)_2$, discussed by L. H. Milligan and G. R. Gillette, W. D. Bancroft, N. R. Dhar, and M. Coblens and J. K. Bernstein. M. L. Nichols and I. A. Derbigny found that the e.m.f. of soln. of the reducing agents with sat. soln. of nitrous acid, and varying amounts of hydrochloric acid, are in agreement with the observations of B. Neumann.

The physiological action of nitrous oxide.—Nitrous oxide has a slight odour, not disagreeable, and a sweetish taste; the aq. soln. also has a sweet taste. The gas may be respired for a short time—say less than four minutes, and it then produces remarkable effects suggestive of intoxication, hysteria, or delirium—particularly if mixed with about one-fourth its vol. of oxygen. There is first great hilarity, and ultimately loss of consciousness. H. Davy,[19] in his *Chemical and Philosophical Researches concerning Nitrous Oxide*, collected a number of observations made on the effects of the gas on different people. In his own case, he said that after breathing 15 quarts of the gas, " I danced about the laboratory as a madman "; and L. Edgworth said that after breathing the gas, " I burst into a violent fit of laughter, and capered about the room without having the power of restraining myself." The early observations of G. Cardone, J. L. Proust, and L. J. Thénard were possibly made with an impure gas, since their sensations were mainly disagreeable. C. Baskerville and R. Stevenson discussed the preparation and purification of this gas for use as an anæsthetic. If the breathing of the gas be continued, the intoxication stage is quickly passed, unconsciousness and insensibility to pain follows. Hence the gas has long been used as an anæsthetic for small surgical operations, dentistry, etc.; but, owing to the unpleasant after-effects sometimes produced, it is not used so much as formerly. If the breathing of the gas be continued still further, death may ensue. The effects on different people are not always the same. H. Wieland attributed the narcotic effect of nitrous oxide to its interference with the utilization of oxygen by the nerve-cells. M. Nussbaum, P. Bert, C. Winkler, and others have studied the use of this gas as an anæsthetic. L. Hermann said that this gas does not form a compound with hæmoglobin, and cannot do the work of oxygen in respiration, the anæsthetic action is attributed by F. Jolyet and T. Blanche to its displacing the dissolved oxygen in the blood. Small birds are killed by the gas in about 30 seconds; dogs and rabbits in 3–4 minutes. J. Bock found that the lowest fatal press. of the gas for rats is 3 atm., and they are killed by paralysis of the respiratory centre in 8–22 minutes. H. Wieland found the vital activities of the round worm are not affected by nitrous oxide. W. Knop found that young shoots of the *typha latifolia* can grow in an atm. of nitrous oxide, and decompose the gas; indeed, F. Hatton thought that the bacteria in a putrefying extract of meat grow better in nitrous oxide than in air.

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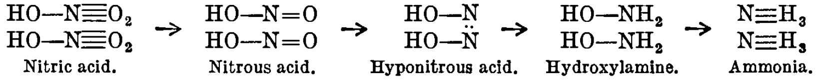
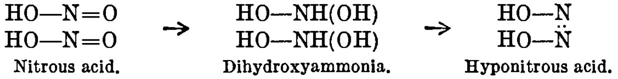
§ 33. Hyponitrous Acid

The reduction of nitrites and nitrates to ammonia readily occurs in alkaline soln. For example, if an excess of sodium or potassium hydroxide be added to nitric acid, the salt is reduced to ammonia by sodium. Intermediate products are formed during the reduction of the nitrate to ammonia. Thus, in 1861, C. F. Schönbein[1] observed the formation of a nitrite when sodium amalgam is the reducing agent, and with the same reducing agent P. de Wilde obtained nitrous oxide, ammonia, and nitrogen as final products. Some years later, E. Frémy, and E. J. Maumené found what was considered to be hydroxylamine among the products of the reduction—a result confirmed later by E. Divers and T. Haga. In 1871, E. Divers discovered the hyponitrites among the products of the reduction, and he also confirmed C. F. Schönbein's observation, for he found a comparatively large proportion of nitrite was sometimes formed during the reduction of nitrates by sodium amalgam. In a general way, E. Divers found that nitrous oxide, N_2O, nitrogen, hydroxylamine, NH_2OH, ammonia, NH_3, sodium hyponitrite, $Na_2N_2O_2$, and sodium hydroxide were always formed during this reaction:



$$\begin{array}{ccccccccc} \text{HO—N}\equiv\text{O}_2 & & \text{HO—N=O} & & \text{HO—N} & & \text{HO—NH}_2 & & \text{N}\equiv\text{H}_3 \\ \text{HO—N}\equiv\text{O}_2 & \rightarrow & \text{HO—N=O} & \rightarrow & \text{HO—}\ddot{\text{N}} & \rightarrow & \text{HO—NH}_2 & \rightarrow & \text{N}\equiv\text{H}_3 \\ \text{Nitric acid.} & & \text{Nitrous acid.} & & \text{Hyponitrous acid.} & & \text{Hydroxylamine.} & & \text{Ammonia.} \end{array}$$

The formation of nitrous oxide and nitrogen is probably the result of secondary or concurrent reactions. According to W. R. Dunstan and T. S. Dymond, the first product of the reduction of sodium nitrite is the hypothetical sodium derivative of *dihydroxyammonia*, $NH(OH)_2$, thus: $2Na+2H_2O+NaNO_2 \rightarrow NaN(OH)_2+2NaOH$; which then condenses to form sodium hyponitrite: $2NaN(OH)_2 \rightarrow 2H_2O+Na_2N_2O_2$; or,



$$\begin{array}{ccccc} \text{HO—N=O} & & \text{HO—NH(OH)} & & \text{HO—N} \\ \text{HO—N=O} & \rightarrow & \text{HO—NH(OH)} & \rightarrow & \text{HO—}\ddot{\text{N}} \\ \text{Nitrous acid.} & & \text{Dihydroxyammonia.} & & \text{Hyponitrous acid.} \end{array}$$

The dihydroxyammonia has not been isolated, and it may or may not be an ephemeral intermediate product. W. R. Dunstan and T. S. Dymond consider that the nitrogen formed in the reduction is the joint effect of hydroxylamine and dihydroxyammonia: $NH_2OH+NH(OH)_2 \rightarrow N_2+3H_2O$. The relative proportions of the reduction products vary greatly within well-defined limits from a maximum down to almost zero.

A maximum yield of *hyponitrites*—eq. to about one-sixth of the total nitrogen—is obtained by using an excess of amalgam, with a conc. soln. (1 : 3) of sodium nitrite, at a temp. below 100°; a maximum yield of *hydroxylamine*—eq. to about 9 per cent. of the nitrogen in the nitrite—is obtained by using a dil. soln. (1 : 50) of sodium nitrite, and keeping the soln. above the amalgam well agitated; to obtain a maximum yield of *nitrous oxide*, the soln. should be kept cool; and for a maximum yield of *nitrogen*, the temp of the soln. should be high; a cold soln. also favours the formation of *ammonia*. Hot dil. soln. give little else than ammonia and nitrogen. So long as any nitrite is present, no hydrogen will appear—except possibly with very dil. aq. soln.

In 1800, H. Davy prepared what he believed to be the potassium salt of nitrous oxide by exposing a mixture of potassium sulphide and hydroxide to nitrous oxide. The sulphide was converted into sulphate, and by solution and crystallization at a low temp., he obtained the compound "mingled with very little potassium carbonate and still less sulphide." The product evolved nitrous oxide when heated, or when treated with carbon dioxide, of sulphuric, hydrochloric, or nitric acid. H. Hess also obtained what may have been silver hyponitrite, by heating barium nitrate, and treating the product with silver salt, and decomposing some of the crystals thus obtained by water.

The preparation of the hyponitrites.—M. L. Nichols and I. A. Derbigny postulated that nitrous oxide in soln. forms hyponitrous acid: $N_2O+H_2O=(HNO)_2$. The several reactions in which hyponitrites are formed can be grouped as follow:

(1) *The reduction of nitrates, nitrites, or nitric oxide.*—In 1871, E. Divers found that when a soln. of sodium nitrite or nitrate is treated with sodium amalgam, the nitrite or nitrate is reduced to sodium hyponitrite: $2NaNO_3+[8H]=4H_2O+Na_2N_2O_2$. The soln. should then be treated with yellow mercuric oxide to destroy the hydroxylamine, and filtered. The alkaline liquid is neutralized by acetic acid, and, when silver nitrate is added, a precipitate of silver hyponitrite, $Ag_2N_2O_2$, is formed. E. Divers prepared sodium hyponitrite by the following process:

Sodium nitrite is dissolved in 3 times its weight of water, and 3 gram-atoms of sodium, in the form of amalgam, per mol of sodium nitrite added in small quantities at a time. The liquid is cooled during the operation. The last quarter of the amalgam is added rapidly, and the flask removed from the cooling bath and agitated. The whole is then violently agitated in a stoppered bottle until a drop of the dil. soln. gives with a drop of silver nitrate and an excess of dil. nitric acid, no blackening due to hydroxylamine. The filtered soln. may smell of ammonia, and this can be removed by exposing the liquid in a dish over sulphuric acid and under reduced press. for a few hours. The liquid is now a conc. soln. of sodium hyponitrite and hydroxide. The filtered soln. when kept at 25°–30° in vacuo over sulphuric acid will deposit the hyponitrite in crystalline granules; if the temp. be below 15°, hydrated sodium hydroxide may be deposited. The hyponitrite may be also precipitated from the soln. by the addition of a large proportion of alcohol.

W. Zorn preferred to use barium nitrite because it is more readily obtained in a state of purity. S. M. Tanatar said the yield is improved if a liquid sodium amalgam is employed. A. Hantzsch and L. Kaufmann found that a 6–7 per cent. yield of silver hyponitrite is obtained if an excess of sodium nitrite be always present. The above process was used by P. de Wilde, and D. H. Jackson. W. Zorn, and E. Divers and T. Haga obtained the hyponitrite when nitric oxide is reduced by an alkaline soln. of stannous chloride: $Sn(OK)_2+2KOH+2NO=K_2SnO_3+H_2O+K_2N_2O_2$; W. R. Dunstan and T. S. Dymond, when an alkali nitrite or nitric oxide is reduced by freshly precipitated ferrous hydroxide suspended in dil. alkali-lye; E. Divers and T. Haga, when hyponitrososulphates are reduced by sodium amalgam; P. C. Ray, when mercuric nitrite is reduced by potassium cyanide: $Hg(NO_2)_2+KCy=HgN_2O_2+2KCyO$—E. Divers had some doubts about this reaction; G. Roederer, when nitric oxide is passed into a soln. of strontium in liquid ammonia, a gelatinous precipitate of strontium hyponitrite is formed which appears as a white powder when the liquid ammonia vaporizes; J. A. Joannis obtained a similar conversion of sodammonium and potassammonium by nitric oxide; E. Weitz and W. Vollmer recommended a soln. of sodium in pyridine: $2Na(C_5H_5N)_2+2NO=Na_2N_2O_2+4C_5H_5N$; and W. Zorn, when alkali nitrites are reduced by electrolysis with a mercury cathode—*e.g.*, barium hyponitrite is formed by the electrolysis of a mixture of equal parts of sodium nitrite and barium acetate with 12 times its weight of water. The reported reduction of nitrites to hyponitrites, by A. E. Menke, by fusion with iron-filings was denied by W. Zorn.

(2) *The condensation of hydroxylamine or of its derivatives with nitrous acid.*—The sodium or silver salt of nitrous acid is usually employed with hydroxylamine chloride or sulphate; the fundamental reaction is symbolized: $NH_2OH+HNO_2=H_2N_2O_2+H_2O$; there is also a secondary reaction resulting in the formation of nitrous oxide: $NH_2OH+HNO_2=N_2O+2H_2O$. S. M. Tanatar warmed potassium nitrite with hydroxylamine chloride at 50° in the presence of calcium hydroxide; the precipitate was decomposed with acetic acid; and the chloride and hyponitrite in the soln. were separated by fractional precipitation with silver nitrate. A. Thum used sodium nitrite, and C. Paal used silver nitrite with hydroxylamine chloride; while W. Wislicenus used hydroxylamine sulphate with sodium nitrite. A. Hantzsch treated a methyl alcoholic soln. of free hydroxylamine with nitrous acid or with nitrous fumes (N_2O_3). A soln. of hydroxycarbaminic acid, HO.CO.NH.OH, in methyl alcohol also gives hyponitrous acid when treated with nitrous acid. L. W. Jones and A. W. Scott obtained sodium hyponitrite by mixing alcoholic soln. of sodium ethoxide (corresponding with 6·62 g. of sodium) and of hydroxylamine hydrochloride (20 g.), cooling, filtering, adding sodium ethoxide soln. (corresponding with 15·4 g. of sodium) to the filtrate, cooling again, and distilling the calculated amount of ethyl nitrite directly into the mixture. The sodium salt is precipitated (yield about 13·5 per cent.).

(3) *The oxidation of hydroxylamine or its derivatives.*—S. S. Kolotoff found that hydroxylamine, NH_2OH, can be oxidized by treatment with sodium hypobromite; A. Thum, by mercuric or silver oxide, or with an alkaline soln. of copper hydroxide; and O. Piloty, by treating hydroxylamine with benzene sulphonic chloride. $C_6H_5.SO_2.Cl$, whereby benzsulphohydroximic acid, $C_6H_5.SO_2.NH.OH$, is formed, and this, when decomposed by treatment with potassium hydroxide, furnishes potassium salts of benzenesulphinic acid, $C_6H_5.SO_2H$, and hyponitrous acid, $H_2N_2O_2$: $2C_6H_5SO_2(NHOH)+4KOH=4H_2O+2C_6H_5SO_2+K_2N_2O_2$. A. Kirschner used the following process:

Fifty grams of hydroxylamine disulphinate—prepared by the action of sulphur dioxide on a soln. of sodium nitrite—are dissolved in 35 c.c. of boiling water. The soln. is cooled by ice, and, while keeping the temp. below 30°, it is mixed with 10 c.c. of a concentrated solution of sodium hydroxide (1 : 1), and 90 c.c. more alkali-lye is then added. The mixture is heated to about 50° for 30–45 minutes, and poured into a litre of water. The undecomposed disulphonate and hydroxylamine are destroyed by adding yellow mercuric oxide, and the clear filtered soln. is made up to four litres and treated with silver nitrate so long as the light yellow silver hyponitrite is precipitated. The precipitate is washed with warm water until it is free from acid.

(4) *The hydrolysis of certain oxyamido-compounds.*—E. Divers and T. Haga showed that hydroxylamido-monosulphonic acid, $HO.NH.HSO_3$, and its salts are hydrolyzed by alkaline soln., forming a sulphite and hyponitrite: $2(HO.NH.HSO_3)+6KOH \rightarrow 6H_2O+2K_2SO_3+K_2N_2O_2$. The hyponitrite is obtained by the following process:

Into a round-bottomed, 250 c.c. flask place 13·8 grms. purified sodium nitrite, 10·6 grms. of anhydrous sodium carbonate, and 58·5 grms. water. When all is dissolved by warming the flask, cool in a mixture of ice and salt, and pass sulphur dioxide through the soln. until the soln. is acid to litmus. Add 0·1 c.c. of sulphuric acid still keeping the temp. below 0° so as to convert the nitrite into hydroximidosulphonate—at higher temp. some nitrilosulphonate is formed. A strong current of air blown through the liquid will remove any sulphur dioxide or nitric oxide present. Warm the soln. to 30° and put in a warm place for a day with the flask corked. Complete hydrolysis to hydroxyamidosulphonate occurs without the formation of hydroxylamine. Add 10·8 grms. of sodium carbonate to neutralize the soln., warming the mixture if necessary to dissolve the salt. Transfer the liquid to a 500 c.c. basin; crush 130–165 grms. of potassium hydroxide in a warm mortar, and grind and dissolve in the liquid in the basin. Let the mixture stand in a warm place for 30 hrs.; if kept over 50 hrs. the quantity of hyponitrite sensibly diminishes. The hyponitrite can be converted into the silver salt so as to separate it from other salts in soln., and the silver hyponitrite afterwards converted into the sodium salt by means of sodium iodide.

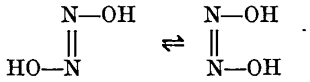
A. Hantzsch found that when dimethyl-nitroso-hydroxy-carbamide, $(CH_3)_2N.CO.N(OH)NO$, or isonitraminecarbamide, is hydrolyzed by alkali-lye at 0°, dimethylamine, carbon dioxide, and alkali hypochlorite are formed. A. Hantzsch and A. Sauer also treated hydroxycarbamide, or dimethylhydroxycarbamide with nitrogen trioxide fumes, and saponified the nitroso-derivatives with alkali-lye. Sodium hydroxide, or sodium ethoxide, was found by H. Wieland to convert styrene pseudonitrosite, $N_2O_2(CHC_6H_5.CH_2.NO_2)_2$, into a mixture of benzaldehyde, nitromethane, alkali hyponitrite, and a little nitrous oxide. It is supposed that the bisnitroso-group is first eliminated producing sodium phenylnitroethanol, $OC_2H_5.CHC_6H_5.CH:NO_2Na$, which further decomposes into benzaldehyde and sodium nitromethane.

The isolation of the free acid.—Although E. Divers prepared various salts of hyponitrous acid in 1871, and W. Zorn prepared the esters—*e.g. diethyl hyponitrite,* $(C_2H_5)_2N_2O_2$—in 1879, anhydrous hyponitrous acid, $H_2N_2O_2$—also called **hyponitrosylic acid**—was not isolated until 1896, when A. Hantzsch and L. Kaufmann obtained it in white crystalline plates, by evaporating the clear soln. obtained by treating silver hyponitrite suspended in dry ether with a soln. of hydrogen chloride in dry ether. Aq. soln. were made by J. D. van der Plaats, in 1877, by treating the silver salt suspended in water, with hydrogen sulphide, hydrochloric, phosphoric, or acetic acid. When an attempt is made to concentrate the aq. soln., it decomposes into water and nitrous acid: $H_2N_2O_2 \rightarrow N_2O+H_2O$. If the dry salt be treated with hydrogen sulphide, the liberated acid is at once decomposed. S. M. Tanatar obtained a soln. of the acid by treating the silver salt, under ether, with hydrochloric acid; on evaporating off the ether, a yellow oil, which did not solidify at —19°, was obtained. This oil was probably a conc. aq. soln., and it often crystallized when allowed to stand in a desiccator under reduced press. When the attempt is made to isolate the acid by the action of hydrogen sulphide on silver hyponitrite, an explosive decomposition occurs.

The properties of hyponitrous acid and the hyponitrites.—The acid forms white crystalline plates which are so unstable that it has not been analyzed. The solid often explodes spontaneously, and also by friction, and by mere contact with solid potassium hydroxide or acid vapours. The solid is readily soluble in water, in alcohol, ether, chloroform, and benzene, but is only sparingly soluble in ligroïn. According to A. Hantzsch and L. Kaufmann, the aq. soln. soon decomposes into water and nitrous oxide; the decomposition is rapid at 25°, and very slow at 0°. J. D. van der Plaats said that if acetic or nitric acid be present, hyponitrous acid can be boiled without decomposition. A. Hantzsch and L. Kaufmann found that the reaction with water is not reversible, and when the rate of decomposition is followed by the usual methods, the results are not in harmony with the equation for a unimolecular reaction, $dx/dt=k(a-x)$, required for $H_2N_2O_2 \rightarrow H_2O+N_2O$, since a number of disturbing side reactions simultaneously occur resulting in the formation of nitric and nitrous acids as well as ammonia. According to A. Hantzsch and L. Kaufmann, the decomposition of hyponitrous acid may occur in three ways: forming in the one case nitrous oxide, $H_2N_2O_2=N_2O+H_2O$; in a second case, hydroxylamine, $3H_2N_2O_2=2NH_2OH+2N_2O$; and in the third case, ammonia, $3H_2N_2O_3=2NH_3+2N_2O_3$. If a reaction catalyzed the third reaction without affecting the first or third, ammonia would be produced without the mediation of hydroxylamine. The electrical conductivity of hyponitrous acid shows that the acid is of about the same strength as carbonic acid, but, as E. Divers showed, it reddens litmus more strongly than carbonic acid, and the colour disappears when the litmus paper is dried. M. Berthelot and P. Petit calculated the heat of formation of hyponitrous acid, in aq. soln., from its elements to be —54·7 Cals. The heat of formation of nitrous oxide is —20·6 Cals., so that in the union of nitrous oxide with water 36·8 Cals. of heat are absorbed. This quantity of heat is greater than the heat of neutralization of hyponitrous acid, and consequently it is not to be expected that nitrous oxide can be converted into a hyponitrite by the action of alkali-lye; but the decomposition of hyponitrites with the evolution of nitrous oxide should be easily effected.

An aq. soln. of hyponitrous acid slowly decomposes into nitrous oxide and water. According to E. Divers, a soln. of one or two grams of acid in a litre of water, at 0°, falls perceptibly in conc. in an hour; and at 25°–30°, it may lose about 17 per cent. of acid in 24 hrs. A. Thum observed a smaller loss. Hyponitrous acid, said E. Divers, is oxidized by nitrous acid, and the stronger oxidizing agents. No way of deoxidizing or hydrogenizing hyponitrous acid is known. It resists attack by sodium amalgam, and, according to A. Thum, by tin and sulphuric acid. W. Zorn said that ethyl hyponitrite is reduced to alcohol and nitrogen by tin and acetic or hydrochloric acid, but since the acid readily decomposes when moist into nitrogen, alcohol, and aldehyde, E. Divers suggested that the alleged reduction is nothing but the hydrogenization of the aldehyde. A. Kirschner said that hyponitrous acid slightly decolorizes iodine-water, but E. Divers showed that this is due to the presence of a trace of sulphite in the acid. According to E. Divers, and A. Thum, a soln. of the free acid does not liberate iodine from potassium iodide. A. Thum said that the acid neither oxidizes hydriodic acid, nor reduces iodine, but J. D. van der Plaats said that starch and potassium iodide test-paper are coloured blue by hyponitrous acid. According to A. Hantzsch and L. Kaufmann, while the pure acid does not liberate iodine from potassium iodide, the mixture liberates iodine after standing some time. This is because the acid breaks down not only into nitrous oxide and water, but it also forms some nitrous acid. Hence, a soln. of silver hyponitrite in conc. sulphuric acid gives the nitrous acid reaction with diphenylamine and ferrous sulphate. J. D. van der Plaats showed that conc. sulphuric acid decomposes hyponitrous acid and its salts, forming nitrous oxide; and A. Hantzsch and L. Kaufmann stated that some nitrogen trioxide and ammonia are formed at the same time: $3H_2N_2O_2=2NH_3+2N_2O_3$; on the other hand, E. Divers, could detect only nitrous oxide and water in the products of the reaction; and A. Hantzsch and A. Sauer added that the nitrogen trioxide and ammonia may have been derived from impurities in the hyponitrite. E. Divers doubts if nitrous acid is ever produced in the spontaneous decomposition of hyponitrous acid. P. C. Ray and A. C. Ganguli showed that hyponitrous acid decomposes simultaneously: $H_2N_2O_2=H_2O+N_2O$, and $5H_2N_2O_2=4H_2O+2HNO_3+4N_2$. The presence of nitric, sulphuric, or hydrochloric acid may have a specific directive influence by favouring one of these reactions; thus, the presence of sulphuric acid gives a larger yield of nitrous oxide. E. Divers found the hyponitrous acid decomposes silver carbonate and possibly also lead and some other carbonates. There is no evidence that carbon dioxide can decompose a hyponitrite. Hyponitrous acid decomposes silver sulphate, nitrate, and chloride. A. Thum said that hyponitrous acid is very stable in the presence of reducing agents. If a soln. of hyponitrous acid be treated with acetic acid and zinc-dust, F. von Brackel recognized the formation of some hydrazine; sodium hydrosulphite also reduces the acid to hydrazine, but not sodium amalgam. Acid or alkaline soln. of potassium permanganate oxidize hyponitrous acid; A. Thum said that in acid soln. nitrous acid is formed, and in alkaline soln., only nitrous acid. A. Kirschner observed that only one gram-atom of oxygen is consumed per mol of hyponitrous acid. Bromine, and hypochlorites also oxidize the acid. M. Coblens and J. K. Bernstein found that when silver hyponitrite is added to an acid soln. of titanous chloride, it is reduced to nitrous oxide but no ammonia is formed; and when the silver hyponitrite is added to an acid soln. of stannous chloride, hydroxylamine is formed. Hence, in the reduction of hyponitrous acid by titanous salts, gases may escape before the reducing agent has a chance to do its full work.

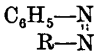
The constitution of hyponitrous acid.—Hyponitrous acid is dibasic. This is illustrated by the mol. wt. determined for the acid by f.p. methods by A. Hantzsch and L. Kaufmann; for ethyl hyponitrite, by W. Zorn; and for the sodium salt, by E. Divers. The dibasicity is further illustrated by the formation of two series of salts: the normal hyponitrites, $R_2N_2O_2$, and the acid hyponitrites or hydrohyponitrites, RHN_2O_2. When an aq. soln. is titrated with alkali, using phenolphthalein as indicator, the red coloration appears when but half the quantity of the base required for the normal salt has been added. These formulæ are also in accord with the analyses. M. Berthelot and J. Ogier's analyses—$Ag_4N_4O_5$ for the silver salt, and N_4O_3 for the anhydride—were probably made with impure materials. According to W. Zorn, the reduction of diethyl hyponitrite with sodium amalgam, or tin and hydrochloric acid, furnishes alcohol with some aldehyde: $(C_2H_5)_2N_2O_2+H_2=N_2+2C_2H_5OH$—*vide supra.* This is taken to show that the ethyl groups are not directly attached to the nitrogen atoms but have intermediate oxygen atoms, $C_2H_5.O.N:N.O.C_2H_5$, otherwise some amine, $C_6H_5.NH_2$, or imide, $(C_2H_5)_2:NH$, would be formed. Hence also the free acid is probably HO.N : N.OH, corresponding with the substitution of the bivalent oxygen of nitrous oxide with two univalent hydroxyl groups. This constitution is also in agreement with the assumption that hyponitrous acid is a *diazohydroxide.* A. Hantzsch argued that because nitramide, $NH_2.NO_2$, is obtained by the hydrolysis of nitrocarbamic acid, $NO_2.NH.COOH$, that is, $HO.CO.N_2O_2H$, and hyponitrous acid is a product of the hydrolysis of isonitraminecarbamide $(CH_3)_2N.CO.N_2O_2H$, as indicated above, therefore nitramide and hyponitrous acid have a similar structure: HO—N=N—OH. Owing to the greater ease with which nitramide and its salts break down with the evolution of nitrous oxide, A. Hantzsch also argues that nitramide in the syn-acid, and hyponitrous acid is the anti-acid. Certainly, the acid character of nitramide is in strong contrast with the other inorganic amides, and the fact that it breaks down into nitrous oxide leaves its structural identity with an assumed amide of nitric acid, *viz.*, $H_2N.NO_2$, an open question. It is therefore conceivable that the molecule may have two different structures represented graphically by



$$\begin{array}{r} \text{N—OH} \\ \| \\ \text{HO—N} \end{array} \rightleftharpoons \begin{array}{l} \text{N—OH} \\ \| \\ \text{N—OH} \end{array}$$

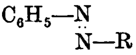
Anti-form. Syn-form.

This means that with our present system of representing the composition of compounds, the hydroxyl groups in hyponitrous acid may be disposed on the same side of the molecule—the **syn or cis** (*cis*, on this side of) **type**; or on opposite sides of the molecule—the **anti or trans** (*trans*, across) **type.** Evidence of the possible existence of organic derivatives of three types are known:



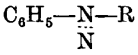
$$\begin{array}{l} C_6H_5\text{—N} \\ \quad R\text{—N} \end{array}$$

Syn-diazo-compounds.



$$\begin{array}{l} C_6H_5\text{—N} \\ \qquad\ \ \text{N—R} \end{array}$$

Anti-diazo-compounds.



$$\begin{array}{l} C_6H_5\text{—N—R} \\ \qquad\ \ \text{N} \end{array}$$

Diazonium-compounds.

The dehydration of the syn-form of hyponitrous acid is supposed by A. Hantzsch to furnish nitrous oxide. H. Henstock gave for the electronic structure:

$$\overset{+}{H}\text{—}\overset{-}{O}\text{—}\overset{+}{N}=\overset{+}{N}\text{—}\overset{-}{O}\text{—}\overset{+}{H}$$

In the analytical determination of the hyponitrites, W. Zorn treated soln. of the free acid, or of its salts in cold dil. nitric acid with an excess of silver nitrate, and just neutralized the free acid with ammonia or sodium carbonate. The washed and dried precipitate was weighed as silver hyponitrite, or weighed as metal or chloride. A. Thum treated the aq. soln. of the acid with an excess of a soln. of permanganate, and in 15 minutes added sulphuric acid; after standing for another hour the soln. was warmed to 30°, and treated with a known quantity of $0{\cdot}1N$-oxalic acid sufficient to decolorize the permanganate. The excess oxalic acid was determined by permanganate titration. A. Hantzsch and A. Sauer, and

A. Kirschner did not obtain good results by the permanganate process, as E. Divers showed, but they did not follow A. Thum's directions closely.

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§ 34. The Hyponitrites

According to A. Hantzsch and L. Kaufmann,[1] if dry ammonia be passed into the ethereal soln. of hyponitrous acid, **ammonium hydrohyponitrite**, $(NH_4)HN_2O_2$, or $NH_4O.N:N.OH$, is formed in colourless crystals which melt with turbulent decomposition at 64°–65°. The salt spontaneously decomposes into ammonia, nitrous oxide, and water. The salt dissolves in water with an alkaline reaction. **Ammonium hyponitrite**, $NH_4O.N:H.ONH_4$, cannot be prepared directly, but D. H. Jackson (1893) made it by treating silver hyponitrite with an alcoholic soln. of ammonium sulphide, and evaporating the filtered liquid in vacuo over sulphuric acid. Ammonium hyponitrite furnishes long needle-like crystals readily soluble in water and in alcohol. W. Zorn, D. H. Jackson, W. Wislicenus, E. Divers, E. Divers and T. Haga, J. A. Joannis, and A. Hantzsch and L. Kaufmann prepared **pentahydrated sodium hyponitrite**, $Na_2N_2O_2.5H_2O$, by methods indicated in connection with the acid. W. Zorn also obtained it by the electrolysis of a soln. of sodium nitrate, or better, sodium nitrite, using a mercury cathode. The hydrated sodium hyponitrite occurs in small crystals; and when deposited from a conc. soln. of alkali hydroxide, it has a granular appearance. The aq. soln. on evaporation in vacuo does not yield crystals. E. Weitz and W. Vollmer obtained yellow crystals of the *enneahydrate*, $Na_2N_2O_2.9H_2O$; and they prepared sodium hyponitrite by the action of soln. of sodium or pyridine on nitric oxide. A. W. Scott prepared non-hygroscopic sodium hypontrite as follows:

> To a sat. soln. of 3·26 grms. of hydroxylamine hydrochloride in anhydrous ethyl alcohol at −5° is added slightly more than the calculated amount of sodium dissolved in the least amount of alcohol. After filtering, 110 c.c. of anhydrous ether and 3·24 grms. of sodium in the minimum amount of alcohol are added to the soln., which is then cooled

to $-5°$ and twice the calculated amount of either amyl or propyl nitrite added. After being kept at $-5°$ for 1 hour, the sodium hyponitrite is collected, washed with alcohol, then with ether, and dried over sulphuric acid in vacuo; the yield is 13·9 per cent.

The anhydrous **sodium hyponitrite,** $Na_2N_2O_2$, is obtained by dehydrating the hydrate in vacuo. There is, at the same time, a slight loss of nitrous oxide. The product resembles magnesia alba. Heat is evolved when the anydrous salt dissolves in water, and it is insoluble in alcohol. The anhydrous salt only slowly takes up water from a soln. of sodium hyponitrite. Heated in a closely covered vessel, it yields nitrogen and sodium oxide mixed with some nitrate: $3Na_2N_2O_2=2N_2+2Na_2O+2NaNO_2$. The salt bears a heat of 300° without decomposing, and then melts and effervesces; glass, platinum, and even silver are freely attacked by the fused mass, and the product hisses when water is added to it. Sodium hydroxide and nitrite are the solid products when the hydrated salt is quickly heated, and nitrous oxide, as well as nitrogen, is given off. Conc. sulphuric acid decomposes the salt, with the production of odourless, white vapours, and no nitrosylsulphate is formed if the sodium salt is pure. The salt, or a fairly conc. soln. of it, effervesces with a dil. acid like a carbonate. It dissolves a little silver hyponitrite and decomposes silver chloride. Dry sodium hyponitrite is not decomposed by carbon dioxide, and, since the hydrated or dissolved salt partly decomposes by interaction with the water, its power of fixing carbon dioxide does not indicate that it is directly decomposable by that substance. The soln., when boiled, decomposes moderately fast into hydroxide and nitrous oxide. If allowed to stand for a day, a trace of nitrite is formed. According to W. Zorn, A. Thum, and A. Hantzsch and L. Kaufmann, the conductivity of the aq. soln. decreases with time owing to the hydrolysis. If the free acid be neutralized with sodium hydroxide using phenolphthalein as indicator, the composition corresponds with **sodium hydrohyponitrite,** $NaHN_2O_2$. The soln. readily decomposes into sodium hydroxide and nitrous oxide.

W. Zorn, J. A. Joannis, E. Divers and T. Haga, and E. Divers prepared **potassium hyponitrite,** $K_2N_2O_2$, by the methods employed for the sodium salt indicated in connection with the preparation of the acid. E. Divers said the preparation of this salt is less satisfactory than is that of the sodium salt. Potassium hyponitrite can be precipitated incompletely from its aq. soln. in the anhydrous form by alcohol, and there is a loss during the washing with alcohol. He also treated silver hyponitrite with the calculated quantity of potassium iodide, and rapidly evaporated the soln. in vacuo, subsequent to precipitation by alcohol. The salt is partially decomposed during these operations. The minute, prismatic crystals of potassium hyponitrite decompose more readily than the sodium salt, but are stable if quite dry; they are soluble in 90 per cent. alcohol, aad sparingly soluble in absolute alcohol. E. Divers observed that aq. soln. of alkali hyponitrites decompose slowly into nitrous oxide and alkali hydroxide—gradually in the cold, rapidly when heated. Alkali hydroxides impede the decomposition, and if in conc. soln., stop it. The neutralization of the alkali by carbon dioxide hastens the decomposition, but this is not due to the decomposition of the hyponitrite by the carbon dioxide. M. Berthelot gave for the heat of neutralization ($H_2N_2O_2$aq., 2KOHaq.)=15·6 Cals. H. Stamm measured the solubility of the sodium salt in aq. ammonia.

E. Divers prepared the basic salt **cupric hydroxyhyponitrite,** $Cu_2(OH)_2N_2O_2$, according to A. Thum. This salt was also made by S. S. Kolotoff, A. Thum, and A. Kirschner. It is obtained by adding sodium hyponitrite to a soln. of a cupric salt. The acid liquor so obtained deposits more salt when neutralized. A small quantity of this salt is precipitated when an excess of cupric sulphate is added to a soln. of hydroxylamine sulphate, and then a little ammonia. The sea-green salt is very stable; it gives water, a mixture of cupric and cuprous oxides, and nitric and nitrous oxides when heated. The salt can be boiled with water without losing its colour, but it is decomposed by a soln. of sodium hydroxide. It is soluble in dil. acids and aq. ammonia. E. Divers tried unsuccessfully to make **cuprous**

hyponitrite by treating sodium hyponitrite with cupric sulphate in the presence of free hydroxylamine. Cuprous oxide is first precipitated, and then by aerial oxidation, the basic cupric hydroxyhyponitrite is formed. S. S. Kolotoff claimed to have made **dihydrated cuprous hyponitrite,** $Cu_2N_2O_2.2H_2O$, by oxidizing hydroxylamine by sodium hypobromite, and treating the product with cupric sulphate. G. T. Morgan and F. H. Burstall obtained evidence of the formation of copper trisethylenediaminohyponitrite, $[Cu\ en_3]N_2O_2$, by the action of silver hyponitrite on copper in the presence of ethylenediamine. E. Divers made **silver hyponitrite,** $Ag_2N_2O_2$, or **nitrosyl silver,** as previously indicated. The salt was also made by W. Zorn, J. D. van der Plaats, H. Wieland, A. Hantzsch and L. Kaufmann, M. Berthelot and J. Ogier, O. Piloty, and E. Divers and T. Haga. The methods employed are indicated in connection with the preparation of the acid. P. Sabatier and J. B. Senderens could not make it by the union of nitric oxide and silver at any temp. tried. E. Divers recommended the following process for preparing silver hyponitrite:

A conc. soln. of sodium hyponitrite and hydroxide is diluted and mixed with sufficient silver sulphate or nitrate in dil. aq. soln. (1 : 210) to precipitate the hyponitrite. The soln. may or may not be neutralized with acetic acid before adding the silver salt. The mixture is stirred vigorously to convert silver oxide into hyponitrite. When the precipitate has nearly all subsided, the turbid liquor of bright yellow is decanted and again treated with the silver salt until, after stirring well, brownish-silver oxide remains. The whole is then mixed and left to settle. A good light is necessary to judge the colours, but light should be avoided as much as possible. The precipitate is washed by decantation, and stirred up with successive portions of dil. sulphuric acid (1 : 250), until the acid fails to become neutral and shows a slight yellow opalescence when mixed with a drop of a soln. of sodium carbonate. The precipitate is then washed by decantation with water until free from sulphate; then with water containing a trace of sodium carbonate; and finally with water. It is then collected on a filter, dried in vacuo, and then heated to 100° in dry air. The salt can be purified before drying by dissolving it in small portions at a time, in ice-cold dil. sulphuric acid (1 : 333); the filtered soln. is made alkaline with sodium carbonate, and the precipitate washed with dil. sulphuric acid, etc., as before. Silver nitrate is employed at the start if it is essential to keep nitrates from the final product; for the washing re-precipitation, etc., are but imperfect means of purifying the precipitate. Sodium carbonate is preferable to aq. ammonia for precipitating the salt because, as A. Hantzsch and L. Kaufmann found, the last trace of ammonia is difficult to wash from the silver salt; and silver carbonate is at the same time excluded because of its solubility in the excess of carbon dioxide always present in the soln.

Silver hyponitrite is bright yellow, and if pale in colour it generally contains a trace of ammonia, or some silver oxide. If black silver suboxide is present, the colour may be greyish-yellow, and with other impurities present, the colour may be bright green. There is no evidence that the difference in colour is due to the presence of allotropic forms. When precipitated from strongly alkaline soln., or from conc. soln. of the sodium and silver salts, the precipitate is compact, and dense, but if precipitated from dil. soln., it is flocculent and bulky. A. Kirschner, and C. Paal and F. Kretschmer, obtained crystals of silver hyponitrite by deposition from the ammoniacal soln., either by evaporation or by dilution with water. M. Berthelot and J. Ogier gave —9·3 Cals. for the heat of formation. E. Divers stated silver hyponitrate is decomposed by a moderate heat into nitric oxide, silver, and a little silver nitrate; it does not fuse or exhibit any change other than the passage from a bright yellow to a silver-white colour. J. D. van der Plaats said that silver hyponitrite decomposes explosively when heated—but, added E. Divers, this preparation probably contained some acetate. A. Thum found that the bright yellow salt when heated becomes brown before assuming the silvery white colour; and A. Kirschner said that it is temporarily black. E. Divers attributes the brown or black coloration to the dense, red, almost opaque fumes of nitrogen peroxide emitted by the decomposing salt, and possibly to the presence of some sulphite. A. Thum detected no silver nitrate among the products of decomposition, but found that nitrogen peroxide is produced. E. Divers then demonstrated that nitrogen, nitric oxide, nitrogen peroxide, silver, silver nitrate, and possibly a trace of nitrite are produced during the decomposition. The first action is represented: $2Ag_2N_2O_2=4Ag+N_2+2NO_2$. The presence of silver nitrate is attributed to the action of nitrogen peroxide on the undecomposed hyponitrite: $Ag_2N_2O_2+4NO_2=2AgNO_3+4NO$; and the silver nitrate and nitric oxide interact: $AgNO_3+NO=Ag+2NO_2$. P. C. Ray and A. C. Ganguli found that the equation: $3Ag_2N_2O_2=4Ag+2AgNO_3+2N_2$ is not supported by analytical data. They represent the action $2Ag_2N_2O_2=2Ag_2O+2N_2O$—with $2Ag_2O=4Ag+O_2$; also $Ag_2N_2O_2=2Ag+2NO$—with $2NO+O=N_2O_3$; $2N_2O_3+Ag=AgNO_3+3NO$; and $5Ag_2N_2O_2=2AgNO_3+(8Ag+2O_2)+4N_2$. The production of the nitrous fumes is thus attributed to a secondary reaction. E. Divers does not accept these conclusions. E. Divers, and A. Kirschner regard the nitrogen peroxide as a direct product of the heating of the salt; and E. Divers assumes nitric oxide to be a product of a series of complex reactions, here it is regarded as a direct product of the decomposition of the hyponitrite.

According to E. Divers, moist silver hyponitrite is not stable, for it very slowly decomposes at ordinary temp.; light and heat quicken the change. The salt thus loses its bright colour, and contains some nitrite and nitrate. The production of a nitrite occurs in a few hours if the salt be exposed to bright diffused light, and in a few minutes in sunlight. When the purified yellow hyponitrite, under water, is exposed to light, a brown flocculent substance is formed on the surface. If a black or grey colour is obtained, impurities were present in the hyponitrite. Silver hyponitrite is least sensitive to light when dry and exposed to dry air. The slight atmospheric oxidation of moist silver hyponitrite observed by E. Divers and T. Haga is attributed by E. Divers to the slow production of nitric oxide which is retained as nitrite and nitrate by the salt, and not to the direct oxidation of the salt. Silver hyponitrite is more soluble in water than silver chloride, and, added A. Thum, the salt is not affected by boiling water. A. Thum, and E. Divers found that the salt is dissolved by dil. nitric or sulphuric acid and can be recovered by quickly neutralizing the acid with alkali. The sulphuric acid soln. soon deposits silver sulphate. Cold acetic acid dissolves silver hyponitrite sparingly; and it is only slightly soluble in phosphoric acid. According to P. C. Ray and A. C. Ganguli, the decomposition of silver hyponitrite by mineral acids at 25°–29° results in the liberation of hyponitrous acid, which then decomposes according to the equation: $H_2N_2O_2=H_2O+N_2O$; and $5H_2N_2O_2=4H_2O+2HNO_3+4N_2$. The products with silver hyponitrite are:

Nitrogen as . . .	N_2	NHO_3	N_2O	Total
Using nitric acid . .	7·25	1·81	1·26	10·32 per cent.
Using hydrochloric acid .	6·95	1·74	1·61	10·30 ,,
Using sulphuric acid . .	4·52	1·13	4·58	10·23 ,,

According to E. Divers, silver hyponitrite is dissolved by aq. ammonia, but only sparingly if dil.; the hyponitrite can be recovered by neutralizing or dissipating the ammonia. Silver hyponitrite is also soluble in soln. of ammonium carbonate or nitrate; in aq. hyponitrous acid; and in a soln. of alkali hyponitrite. Silver hyponitrite is readily oxidized by conc. nitric acid; conc. sulphuric acid acts energetically, and the heat of the reaction is sufficient to decompose some of the salt, forming nitrosyl sulphate, and nitrogen peroxide. The salt is not decomposed by a cold soln. of sodium carbonate; it is not decomposed by a cold dil. soln. of sodium hydroxide; it is completely decomposed by an eq. amount of a soln. of potassium iodide; it is imperfectly decomposed by a soln. of sodium chloride unless in considerable excess—when a soln. of sodium chloride is shaken with an excess of silver hypochlorite, decomposition ceases when the soln. contains 4 eq. of sodium chloride to 5 eq. of sodium hyponitrite; the addition of absolute alcohol effects a partial separation of the two sodium salts. According to A. Thum, silver hyponitrite absorbs dry hydrogen sulphide at 0° without giving off any water or gas; but after some time, an explosive decomposition occurs with the production of light and heat, and the evolution of reddish-brown fumes. Hydrogen sulphide, and phosphoric acid set free hyponitrous acid. It is not attacked by acetic acid; and carbon dioxide does not decompose it.

W. Zorn, A. Kirschner, and E. Divers prepared **tetrahydrated barium hyponitrite,** $BaN_2O_2.4H_2O$, by adding barium chloride to a conc. soln. of sodium hyponitrite; and A. Guntz and R. C. Mentrel found that what was assumed to be the hyponitrite is formed when a soln. of barium in liquid ammonia at —50° is treated with nitrogen peroxide. On dissipating the ammonia, the gelatinous precipitate dries to a white powder. The product was hydrated by exposure to moist air, and decomposed by water with the evolution of nitric oxide. The crystals are but sparingly soluble in water, and are slowly decomposed by cold water, rapidly by hot water. Carbon dioxide of the atm. decomposes the dry salt. It is readily soluble in dil. acetic acid, and when the acid is neutralized by ammonia or baryta-water, the salt is precipitated unchanged. L. Maquenne suspended silver hyponitrite in water, and added enough nitric acid to dissolve about one-third the hyponitrite; the mixture was then agitated with a soln. of barium chloride. The precipitate was filtered and washed; and the filtrate treated with ammonia to obtain more hyponitrite. The precipitate was washed with alcohol, then with ether, and finally dried over sulphuric acid. A. Kirschner mixed ammoniacal soln. of silver hyponitrite and barium nitrate, and washed the precipitate with alcohol and ether. The product corresponded with **hydrated barium hyponitrite,** $BaN_2O_2.H_2O$. W. Zorn obtained **barium hydrohyponitrite,** $BaH_2(N_2O_2)_2$, by adding the calculated quantity of sulphuric acid to barium hyponitrite suspended in water; or by neutralizing the acid with baryta-water and rapidly evaporating under reduced press. The salt readily decomposes with the evolution of nitrous oxide, and the product is accordingly impure. The needle-like crystals are very soluble in water. G. Roederer, as indicated in connection with the acid, obtained **strontium hyponitrite,** SrN_2O_2, by the action of nitric oxide on a soln. of strontium in liquid ammonia. The gelatinous precipitate furnishes a white powder when the ammonia is dissipated. A. Kirschner, and L. Maquenne also prepared **pentahydrated strontium hyponitrite,** $SrN_2O_2.5H_2O$, by the methods employed for the hydrated barium salt. L. Maquenne said that the strontium salt is more stable than the calcium salt, and gives off no gas in vacuo at 100°; it loses water less readily than the barium salt, and, unlike L. Maquenne, A. Kirschner could not obtain the anhydrous salt by heating the hydrate to 100°. L. Maquenne, A. Kirschner, and E. Divers prepared **tetrahydrated calcium hyponitrite,** $CaN_2O_2.4H_2O$, by the methods they employed for the barium salt. L. Maquenne said that the dry salt does not decompose at 100°, but the moist salt slowly decomposes at that temp. It is very sparingly soluble in water, soluble in dil. acids, and in acetic acid, whilst ammonia re-precipitates the unchanged salt from acid soln. The salt is decomposed by sulphuric acid (1 : 1), with the evolution of gas. On account of its stability, E. Divers said that it is a good hyponitrite to keep in stock.

A. E. Menke observed a white precipitate of **magnesium hyponitrite** when a magnesium salt is treated with sodium hyponitrite; **zinc hyponitrite** is formed in an analogous way. Both salts are soluble in acetic acid. According to E. Divers, if sodium nitrite be reduced with sodium amalgam, and neutralized with acetic acid, a greyish-black deposit of mercury is formed on the addition of mercurous nitrate, and not mercurous hyponitrite. This is due to the presence of hydroxylamine with the hyponitrite soln. E. Divers said that **mercurous hyponitrite,** $Hg_2N_2O_2$, is precipitated by adding a soln. of sodium hyponitrite, free from hydroxylamine, to a soln. of mercurous nitrate as in the case of mercuric hyponitrite. P. C. Ray added that the sodium hyponitrite soln. should be neutralized since the precipitate will otherwise be contaminated with mercurous oxide. A. Thum treated the mercurous nitrate soln. with acid potassium hyponitrite; and P. C. Ray obtained it by adding a dil. soln. of sodium hyponitrite to a soln. of mercurous and mercuric nitrites, and obtained a flocculent yellow precipitate of mercurous hyponitrite. No oxide is precipitated from the soln. of mercurous nitrite soln

The bright yellow salt is washed by suction, and dried over sulphuric acid. E. Divers found that the salt is stable, but is blackened by light. A. Thum said that it is blackened in direct sunlight owing to the separation of mercurous oxide. When heated, E. Divers said that it is decomposed, forming mercuric salt, and when further heated, it decomposes like the mercuric salt: $Hg_2N_2O_2=2Hg+2NO$; $Hg_2N_2O_2=Hg+HgO+N_2O$; or $3Hg_2N_2O_2=4Hg+2HgNO_3+2N_2$. A. Thum said that the salt blackens at a little below 100°, and at a higher temp., forms red mercuric oxide. P. C. Ray and A. C. Ganguli found that mercurous hyponitrite begins to decompose slowly at 80°, and on raising the temp. it assumes a black colour, and at 150°, becomes reddish-yellow and decomposition ceases; the temp. can then be raised to 200° without the production of any visible nitrous fumes. There is no evidence that the decomposition proceeds: $Hg_2N_2O_2=2HgO+N_2$, for the actual proportion of nitrogen produced is very small. The main products are mercury and mercuric oxide with nitric and nitrous oxides—the proportion of nitrogen and mercurous nitrate is small and probably an effect of secondary reactions. Thus:

Nitrogen as . . .	N_2	N_2O	NO	Total
Per cent.	0·47	2·22	2·65	6·03

P. C. Ray and A. C. Ganguli represent the reaction as a kind of tautomeric process, half the oxygen being oxylic, Hg.O.N : N.O.Hg=Hg_2O+N_2O and $Hg_2O=HgO+O$; and half imidic, Hg.N : O=Hg+NO. The actual amount of nitrogen formed is almost equal to that existing as mercurous nitrate so that the reaction: $4Hg_2N_2O_2=2HgNO_3+6Hg+N_2+2N_2O$ is more likely than the simpler one: $3Hg_2N_2O_2=2HgNO_3+4Hg+2N_2$. E. Divers said that mercurous hyponitrite is blackened even by very dil. soln. of alkali hydroxides, and it dissolves readily in dil. nitric acid, and can be re-precipitated from the soln. by cautious neutralization with sodium carbonate. According to P. C. Ray, the nitric acid soln. of mercurous hyponitrite immediately becomes opalescent from the separation of mercury which remains at first in a fine state of suspension; if, however, the soln. be set aside for an hour or so, the mercury settles at the bottom, and there is a slow and continuous effervescence owing to the liberation of nitrous oxide; consequently, the salt is partially decomposed in the nitric acid soln.: $Hg_2N_2O_2=Hg+Hg(NO)_2$, and that when the nitric acid soln. is treated with alkali-lye some mercurous oxide is precipitated. P. C. Ray and A. C. Ganguli found that on the decomposition of the salt by the action of nitric, hydrochloric, and sulphuric acids, as in the case of silver hyponitrite, the hyponitrous acid is liberated and decomposed according to the simultaneous equations: $H_2N_2O_2=N_2O+H_2O$; and $5H_2N_2O_2=4H_2O+2HNO_3+4N_2$. The percentage composition of the gases with the different acids was:

Nitrogen as . . .	N_2	NHO_3	N_2O	Total
Using nitric acid . .	3·55	0·89	0·56	5·0
Using hydrochloric acid .	3·76	0·94	1·51	6·21
Using sulphuric acid . .	1·60	0·40	2·98	4·98

so that the presence of the mineral acid has a specific directive influence in determining the course of the reaction. E. Divers explained the incompleteness of the decomposition with sulphuric acid by the low solubility of the mercurous sulphate. He said nitric oxide, and nitrogen trioxide or peroxide are produced by the oxidizing action of the less stable oxides.

According to E. Divers, normal **mercuric hyponitrite**, HgN_2O_2, is obtained by precipitation from sodium hyponitrite and mercuric nitrate. The mixed soln. of sodium hydroxide and hyponitrite obtained by reducing sodium nitrite with sodium amalgam is diluted and almost neutralized by dil. nitric acid keeping the soln. ice-cold all the time. It is then poured into a soln. of mercuric nitrate which must not be in excess, and should contain as little free acid as possible. The slightly turbid mother-liquor is decanted from the precipitate, and, after being neutralized with sodium carbonate, is mixed with more mercuric nitrate, and poured back on the main precipitate; after agitation the mixture is allowed to settle, and the mother-liquor decanted off the precipitate which should be washed quickly by decantation since it is liable to be quickly destroyed by the acid mother-liquor. Mercuric hyponitrite is a flocculent, cream-coloured precipitate, which is easily washed on the filter, and dries to a pale, buff powder—the colour is probably due to an incipient change to the mercurous salt. If dried on a porous tile, it seems to be *trihydrated*, $HgN_2O_2.3H_2O$, but if dried in a desiccator it is anhydrous. The salt is sensitive to light and should be dried in the dark. A soln. of mercuric nitrite or chloride, however highly dilute, always yields mercuric hyponitrite, when treated with sodium hyponitrite in the presence of potassium sulphate, whereas mercuric nitrate under similar conditions gives the basic sulphate, $2HgO.HgSO_4.\frac{1}{2}H_2O$. P. C. Ray, therefore, assumes that the nitrogen is attached to the mercury in the nitrite, but in the nitrate, it must be united to oxygen. Mercuric hyponitrite is decomposed by heat into mercuric oxide, and nitrous oxide, and also into metal and nitric oxide. It dissolves in hydrochloric acid, and in sodium chloride soln., but, being unstable, it changes into the mercurous salt so that the soln. is liable to become turbid. P. C. Ray showed that dil. hydrochloric acid readily dissolves mercuric hyponitrite in the cold, and the salt is re-precipitated when the soln. is neutralized by an alkali. Potassium hydroxide at once decomposes mercuric hyponitrite into oxide without forming basic salts; in very dil. alkali-lye, the precipitate is slightly soluble. P. C. Ray found that mercuric hyponitrite dissolves with difficulty as such in dil. nitric acid, and with still greater difficulty in boiling conc. nitric acid, the hyponitrite is re-precipitated on adding an alkali. Slowly or quickly, mercuric hyponitrite decomposes into mercurous hyponitrite and nitric oxide, and some of the latter is oxidized by air converting some hyponitrite into nitrate. E. Divers added that no other mercuric salt decomposes into the mercurous salt, although many cupric salts change to cuprous salts; ferric oxalate also changes to ferrous oxalate and carbon dioxide. P. C. Ray described some basic mercuric hyponitrites; thus trihydrated **mercuric trioxyhyponitrite,** $3HgO.HgN_2O_2.3H_2O$, or $3Hg(OH)_2.HgN_2O_2$, is formed by dropping a very dil. soln. of sodium hyponitrite (free from hydroxylamine) to a mixed soln. of mercurous and mercuric nitrites containing sodium chloride to eliminate the mercurous mercury. If the order of mixing be reversed, or if too much hyponitrite be used at once, the precipitate turns grey or even black. The flocculent yellow precipitate was washed and dried. It is also obtained by adding a soln. of sodium hyponitrite to one of mercuric chloride. The yellowish powder is sparingly soluble in dil. or conc. nitric acid, and easily soluble in warm dil. hydrochloric acid. The pentahydrate was obtained by adding a soln. of sodium hypochlorite to a soln. of mercuric nitrate containing as little as possible free nitric acid. Pentahydrated **mercuric pentoxytrihyponitrite,** $5HgO.3HgN_2O_2.5H_2O$, or $5Hg(OH)_2.3HgN_2O_2$, was obtained by adding potassium cyanide to a neutral soln. of mercurous and mercuric nitrates mixed with just enough sodium chloride to remove mercurous mercury, but no chloride should be in excess: $Hg(NO_2)_2+KCy=HgN_2O_2+2KCyO$. The precipitate is washed with water, and dried in darkness over sulphuric acid. The soln. of the salt in warm dil. hydrochloric acid, when neutralized with alkali hydroxide, gives a voluminous precipitate.

A. E. Menke found **aluminium hyponitrite** is formed as a white precipitate when sodium hyponitrite is added to a soln. of an aluminium salt. It is insoluble in water, and in acetic acid. The precipitate of **cerium hyponitrite** obtained in an analogous way is soluble in acetic acid; likewise also **tin hyponitrite,** which is insoluble in acetic acid; and lead hyponitrite. E. Divers, A. Thum, and A. Kirschner prepared **lead hyponitrite,** PbN_2O_2, by the action of a soln. of sodium hyponitrite on a lead salt. The precipitate at first is cream coloured and flocculent, but it soon becomes sulphur-yellow, and the dense, cream-coloured salt is probably a hydrate; A. Kirschner, said E. Divers, mistook it for a basic salt *lead oxyhyponitrite*, $PbO.PbN_2O_2$. A. Thum found that when formed in a dil. acid soln., the salt is crystalline. It is soluble in dil. nitric acid, and decomposed by sodium hydroxide, but not by a cold soln. of sodium carbonate.

A. E. Menke prepared **bismuth hyponitrite** as a white precipitate by adding sodium hyponitrite to a soln. of a bismuth salt. It is insoluble in acetic acid. The analogous precipitates of white **manganese hyponitrite,** red **cobalt hyponitrite,** and of green **nickel hyponitrite** are soluble in acetic acid. With ferrous salts, olive-green **ferrous hyponitrite** is formed, it is insoluble in water, and becomes yellow when treated with acetic acid. With ferric salts, yellow **ferric hyponitrite** is formed—insoluble in water, soluble in acetic acid. With potassium salts, **platinum hyponitrite** is formed which is less soluble in acetic acid than it is in water.

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§ 35. Nitric Oxide

Early in the seventeenth century, J. B. van Helmont[1] obtained a *spiritus sylvestris* by the action of nitric acid on the metals, he also applied the same name to carbon dioxide; but it is scarcely conceivable that he could have considered the two gases to be the same form of matter even though they were parts of the general chaos. About the middle of the seventeenth century, J. Mayow also prepared the same gas by the action of nitric acid on iron, but he did not study its specific properties; a similar remark applies to C. Huyghens and N. Papin, who made it by the action of nitric acid on copper; and to R. Boyle, who made it by the action of nitric acid on iron or silver and mentioned that it forms red fumes by contact with atm. air. This was confirmed by G. E. Stahl at the beginning of the eighteenth century. S. Hales prepared the gas by the action of nitric acid on mercury, iron-filings, or pyrites. J. Priestley, however, is generally credited with the discovery of the gas. It is true that he prepared it by the action of nitric acid on copper as others had done previously, but he showed that the gas has a number of specific properties and is veritably a chemical individual. He also employed its property of reacting with the oxygen of the atmosphere to form a soluble gas in the volumetric analysis of air (*q.v.*). In **1777**, A. L. Brongniart prepared the gas by the action of nitric acid on organic substances. J. Priestley called the gas *nitrous air;* and both he, and F. Fontana regarded the gas as nitric acid surcharged with phlogiston. H. Cavendish showed that the gas contained oxygen and nitrogen; and at the beginning of the nineteenth century, its composition was established by H. Davy, and J. L. Gay Lussac and L. J. Thénard. In conformity with the antiphlogistic notation, the gas was called *oxyde d'azote*, or **nitric oxide**, NO.

The preparation of nitric oxide.—Nitric oxide is usually regarded as the first product of the oxidation of nitrogen although under certain conditions nitrous oxide (*q.v.*) may be formed. W. Manchot [2] found that it is produced along with ozone by the silent electric discharge in air, and that its production lowers the yield of ozone. It is formed under numerous other conditions. Thus, F. Fischer and H. Marx, W. Nernst, W. Muthmann and H. Hofer, and F. Haber and co-workers obtained it along with ozone when air is led over a glowing Nernst's filament; or past the high potential, alternating current arc; by electric sparks in air; by white-hot surfaces; and by burning hydrocarbons, carbon monoxide, or hydrogen. A. Reis found nitric oxide in the ammonia-oxygen flame. A. Wolokitin found that by working at a press. of 20 atm., a greater proportion of nitric oxide is produced than when the press. is normal. H. Kämmerer found that it is also produced when magnesium burns in air—*vide supra*, fixation of nitrogen. O. F. Tower obtained traces of nitric oxide when a mixture of nitrogen and water vapour is passed over a Nernst's filament at about 2000°. This subject has been discussed in connection with the fixation of nitrogen. The formation of nitric oxide during the oxidation of hydrogen cyanide, in the presence of a platinum catalyst, has been discussed by J. Zawadzky and J. Wolmer, and L. Andrussoff. R. Hara and H. Shinozaki found that with a platinum catalyst a maximum yield of 85 to 95 per cent. is obtained at 800°. The oxidation begins at about 500°. The best conc. of hydrogen cyanide is 4 to 8 per cent.; higher conc. give solid products—cyamelide and cyanuric acid—as well. It is supposed that the hydrogen cyanide, HCy, is first oxidized to cyanic acid, HCyO, and, on further oxidation, this forms water, carbon monoxide, and nitric oxide. If there is a shortage of oxygen, the cyanic acid polymerizes to $(HCyO)_3$ or $(HCyO)_n$. The formation of nitric oxide by the oxidation of ammonia is discussed in connection with that gas. I. Milner obtained nitric oxide during the oxidation of ammonia (*q.v.*) by manganese dioxide, ferric oxide, etc. B. Tacke, and A. J. Lebedeff found nitric oxide to be formed by the action of the *bacterium hartlebii* on nitrates. F. Wöhler found that nitric oxide is produced by heating a mixture of boron nitride and a metal oxide. U. Sborgi and co-workers found that the yield of nitric oxide obtained varies greatly with these different samples and also with the nature of the admixed oxide. With the oxides Fe_2O_3, Ni_2O_3, Co_2O_3, MnO_2, Mn_3O_4, and CuO, yields as high as 72 per cent. are given, and the residue remaining after the reaction gives an increased yield of nitric oxide with a fresh quantity of boron nitride; this result is repeated four or five times, the yield increasing each time until the residue becomes converted into a compact mass.

Nitric oxide is formed during the electro-reduction of nitric acid; G. Brüning employed a current of 5 to 10 amps. at ordinary temp. with nitric acid of 20 to 30 per cent. concentration, according to the electrodes and other conditions employed. At higher temp., nitrogen peroxide is simultaneously produced, and by varying the conditions other products can be obtained. Nitric oxide is also formed, by treatment of nitric acid, nitrous acid, or nitrogen peroxide with reducing agents like carbon, phosphorus, sulphur, organic compounds, many metals, the lower oxides of the metals, and metal salts. It is also formed when nitrogen peroxide is treated with water; or when nitrogen peroxide is heated above 600°. F. Raschig obtained it as a product of the action of nitrous oxide on nitrous acid, and F. Emich, by the action of a mixture of sulphuric acid with 2 per cent. of sodium nitrite on mercury. L. Moser recommended this process, and also the reduction of nitrous acid with hydriodic acid. The gas can be purified by absorbing it in a conc. soln. of ferrous sulphate, and driving it out again by gentle heat. The gas can also be absorbed by a soln. of potassium permanganate or dichromate. R. W. Gray purified nitric oxide by the fractional distillation of the liquefied gas. Nitric oxide is usually prepared by the reduction of nitric acid. Thus,

N. A. E. Millon obtained it by the action of copper, bismuth, lead, silver, or mercury on nitric acid of sp. gr. 1·2 to 1·3. The more dil. the acid, the lower the temp. at which it reacts, and the less is the gas contaminated with free nitrogen. Copper treated with dil. nitric acid under conditions where the rise of temp. is prevented by a freezing mixture, yields a gas so pure that it is all absorbed by a soln. of ferrous sulphate. The reaction between nitric acid and copper was studied by J. H. Niemann, etc.—*vide* the action of this acid on the respective metals. The preparation of nitric oxide by the action of copper on nitric acid has been discussed by L. Carius, A. Senier, H. Kämmerer, J. J. Acworth, and H. Moissan. The initial and final products of the reaction are represented by $3Cu+8HNO_3=3Cu(NO_3)_2+4H_2O+2NO$. G. Lunge said that nitric oxide is almost the only gaseous product obtained by the action of nitric acid of sp. gr. 1·2 on arsenic trioxide. Ferrous sulphate reacts with warm nitric acid, or a mixture of sodium nitrate and dil. sulphuric acid, forming nitric oxide. M. Coblenz and J. K. Bernstein found that nitric oxide is formed, but no ammonia, when sodium nitrite is added drop by drop to an acid soln. of titanous chloride, and when nitric acid is treated with a soln of stannous chloride containing a drop of ferrous sulphate. J. Pelouze, and J. L. Gay Lussac obtained nitric oxide by the interaction of potassium nitrate and a warm soln. of ferrous chloride in dil. hydrochloric acid : $2NaNO_3+6FeCl_2+8HCl=6FeCl_3+2NaCl+4H_2O+2NO$.

J. Thiele said that fairly pure nitric oxide is produced when a conc. soln. of sodium nitrite is dropped into a hydrochloric acid soln. of ferrous chloride or sulphate. Since commercial sodium nitrite usually contains some carbonate, it is recommended that this impurity be removed by treating the soln. with calcium chloride. J. Matuschek found that with a mixture of soln. of sodium nitrite and ferric chloride, nitrogen peroxide and nitric oxide are formed, and that by passing the mixed gases through water the nitrogen peroxide is decomposed into nitric acid and nitric oxide: $FeCl_3+3NaNO_2=3NaCl+Fe(NO_2)_3$, and $2Fe(NO_2)_3+3H_2O=2Fe(OH)_3+3NO_2+3NO$. If the sodium nitrite be placed under carbon disulphide, and a suspension of hydrated ferric chloride in the same solvent be added, the nitrogen peroxide which is formed remains dissolved in the carbon disulphide. L. Moser recommended preparing the gas of a high degree of purity by reducing with mercury a soln. of nitrous acid in sulphuric acid, or by allowing nitrous and hydriodic acids to interact. W. A. Noyes said that nearly pure nitric oxide is rapidly generated by dropping conc. sulphuric acid on to sodium nitrite covered with two or three times its weight of water: $3HNO_2=HNO_3+2NO+H_2O$. By washing the gas with conc. sulphuric acid or water the trace of nitrogen dioxide present is removed. C. M. van Deventer dropped a mixture of potassium nitrite and ferrocyanide into dil. acetic acid: $K_4FeCy_6+HNO_2+CH_3COOH=K_3FeCy_6+H_2O+CH_3.COOK+NO$. R. Weber obtained nitric oxide of a high degree of purity by passing sulphur dioxide into warm nitric acid of sp. gr. 1·15 : $2HNO_3+3SO_2+2H_2O=3H_2SO_4+2NO$. A. Wagner obtained nitric oxide by the action of acids on a mixture of potassium nitrate and sodium sulphite ; and by heating a mixture of potassium nitrate and carbonate in the presence of chromic oxide, manganese oxide, cuprous oxide, or stannous oxide; and M. Chikachigé, by heating a soln. of cobalt nitrate and potassium thiocyanate. S. Abe and R. Hara found that cyanogen can be readily oxidized to nitric oxide by air in the presence of platinum as a catalytic agent.

The physical properties of nitric oxide.—Nitric oxide is a colourless gas at ordinary temp. R. W. Gray said that the liquid is blue ; but K. Adwentowsky[3] found liquid nitric oxide to be colourless in thin layers, but light blue in thick layers, but it is thought that its blue colour is due to the presence of traces of nitrogen trioxide which cannot be removed by fractionation. The liquid can be frozen to a colourless, or a snow-like solid. T. Thomson gave 1·041 for the **relative density** of the gas ; F. Delaroche and J. E. Bérard, 1·0888 ; and H. Davy, 1·093 ; more recent determinations by G. Daccomo and V. Meyer gave 1·0372 ; P. A. Guye and

C. Davila gave 1·0367. The literature was reviewed by M. S. Blanchard and S. F. Pickering. K. Adwentowsky found the **specific gravity** of the liquid at the b.p. is 1·269. R. W. Gray found the **weight of a litre** of nitric oxide gas at n.p. θ to be 1·3402 grms.—the observed data varied from 1·3398 to 1·3408 grms. G. D. Liveing and J. Dewar gave 1·255 for the **specific gravity** of the liquid at the b.p. J. S. Stas found the **molecular weight** to be 29·97 ; P. A. Guye and C. Davila, 30·012. H. Henstock, R. T. Birge, and A. O. Rankine discussed the **electronic structure.** T. Graham, F. Exner, W. Sutherland, A. Naumann, and J. H. Jeans calculated the mol constants at 0°. The **molecular velocity** is 43,900 cms. per sec. ; the **free path,** 903×10^{-8} cm. ; and the **molecular diameter,** 16×10^{-9} cm. to 26×10^{-9} cm. A. Balandin found the mol. vol. to be 23·6 ; and E. Rabinowitsch gave 23·7. E. Moles, G. Kirsch, and P. N. Pavloff studied this subject.

T. Graham gave 0·0001645 for the **viscosity** of the gas at 0°, and 0·0001860 at 20° ; O. E. Meyer and F. Springmühl, 0·000168. H. Vogel studied this subject. A. Klemenc and W. Remi found 0·0001797 at 0°, and for Sutherland's constant, $C=162{\cdot}2$. O. E. Meyer gave 0·878 (oxygen unity) between 10° and 20°. T. Alty studied the surface phenomena of bubbles of nitric oxide in water. A. Masson found the **velocity of sound** in nitric oxide to be 325 metres per sec. ; W. Heuse, 323 metres per sec. A. Jaquerod and O. Scheuer found the divergence of the **compressibility** of the gas from Boyle's law is very slight. The value of a in $1-p_1v_1/p_0v_0=a(p_1-p_0)$ is 0·00097 for oxygen, 0·00117 for nitric oxide, and 0·01527 for ammonia. J. Batuecas gave 0·0000147 for the compressibility of the gas, and 1·00112 for the divergence from Avogadro's law, $1+\lambda$. J. Briner and co-workers observed :

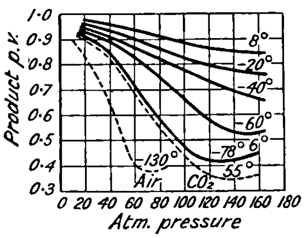


FIG. 70.—Isothermal pv Curves of Nitric Oxide.

	p . . .	30	50	70	90	110	130	150	160
$\dfrac{pv}{p_0v_0}$	9° .	0·9625	0·938	0·9135	0·892	0·862	0·8545	0·843	0·8375
	20° .	0·9475	0·9135	0·8805	0·8455	0·8135	0·787	0·767	0·758
	40° .	0·9365	0·8895	0·8385	0·789	0·7475	0·711	0·6745	0·659
	78·6° .	0·893	0·779	0·6420	0·520	0·441	0·424	0·4435	0·4525

The results are plotted in Fig. 70. When compared with the isotherms of nitrogen, oxygen, carbon dioxide, or ethylene, there is no indication of abnormal polymerization. The subject was studied by C. Schlatter. The **vapour pressure** of solid nitric oxide at —160·6° is 168 mm. According to K. Adwentowsky, the vap. press., p, at different temp. are as follow :

	Solid.			Liquid.				
	−174·4°	−169·2°	−161·0°	−160·6°	−157·8°	−154·1°	−150·9°	−150·2°
p mm.	23	55	158	168	353	519	664	760

and from this temp. on to the critical temp., —92·9° :

	−128·2°	−124·0°	−118·7°	−112·6°	−107·8°	−102·9°	−97·3°	−92·9°
p atm.	8·95	10·7	15·8	21·6	31·0	41·0	53·1	64·6

He said that the vap. press. curve of liquid nitric oxide is somewhat anomalous, and this is attributed to polymerization of the molecules at low temp. The fact that the vapour density at atmospheric press. is quite normal at these temp. indicates, however, that the dissociation of the polymerized mols. is practically complete at this pressure. The high density of the liquid at its b.p., 1·269, is cited as evidence in support of the view that the liquid mols. are associated. W. Nernst's value for the **chemical constant** is about 3·7 ; J. R. Partington's, 1·263 ; F. A. Henglein, and A. Langen, 0·92 ; and A. Eucken and co-workers gave 0·03 for the integration constant of the thermodynamic vap. press. equation ; and A. Eucken and F. Fried, 0·95 for the constant in the equilibrium equation for $2NO=N_2+O_2$.

For the constants in the **equation of state,** $(p+a/v^2)(v-b)=RT$, F. Guye and L. Friedrich gave $a=0{\cdot}00257$ and $b=0{\cdot}00115$ when in terms of the initial vol.; $a=1{\cdot}29\times10^{-6}$ and $b=25{\cdot}9$ if expressed in mols; and $a=1430$ and $b=0{\cdot}862$ if expressed in grams. M. F. Carroll studied the equation of state.

K. Adwentowsky found the coeff. of **thermal expansion** at 760 mm. between —140° and 0° is 0·0037074. H. V. Regnault's value for the **specific heat** of nitric oxide is $c_p=0{\cdot}231$ between 13° and 172°, and it increases with rise of temp. R. Threlfall held it possible that at low temp. some molecular complexes decompose, and they are resolved into the simple molecules at higher temp. G. Daccomo and V. Meyer said that at low temp., —70°, the gas is monomolecular. A. Eucken and E. Karwat gave for the **molecular heat:**

	−250·6°	−239·30°	−194·10°	−177·00°	−168·7°	157·6°	−156·0°
C_p . .	2·04	3·48	7·17	8·49	8·95	17·00	17·5
	Solid.					Liquid.	

K. Scheel and W. Heuse found for the mol. ht., $C_p=7{\cdot}23$; and $C_v=5{\cdot}25$ at 15°; and at —45°, —55°, —80°, W. Heuse obtained $C_p=7{\cdot}14$, 7·22, and 7·28 respectively; and $C_v=5{\cdot}15$, 5·24, and 5·29 respectively. A. Masson gave for the ratio of the two sp. hts., $\gamma=1{\cdot}399$ at 0°; and J. R. Partington and W. G. Shilling, 1·400 at 7·6°. W. Heuse obtained 1·38 at 15° and 1·38 at —80°. J. L. Pickering, and S. W. Saunders discussed the sp. ht. of nitric oxide. The sp. ht. of nitric oxide, calculated by E. E. Witmer from spectroscopic data, is $1{\cdot}33R$ at 50° K., where R is the gas-constant, 1·986 cals. per degree. W. G. Shilling gave:

T° K.	300°	500°	1000°	1500°	2000°	2500°	2700°
C_v . . .	5·00	5·06	5·30	5·73	6·26	6·66	6·73
C_p . . .	7·00	7·05	7·29	7·71	8·24	8·65	8·72
γ . . .	1·399	1·393	1·375	1·347	1·317	1·298	1·295

He also gave $C_v=5{\cdot}102-0{\cdot}0_3564T+0{\cdot}0_69554T^2-0{\cdot}0_91934T^3$.

Nitric oxide was not liquefied by M. Faraday at —110° and 50 atm. press.; but M. Berthelot liquefied it at —11° and 104 atm. press., but not at 8° under a press. of 270 atm. He therefore thought that the **critical temperature** is between —11° and 8°. On the other hand, K. Olschewsky found the critical temp. to be —93·5°, and the **critical pressure,** 71·2 atm.; and K. Adwentowsky gave respectively —92·9° and 64·6 atm. K. Olschewsky found the **boiling point** to be —153·6° at one atm. press., and in addition:

Press. .	71·2	49·9	20·0	10·6	5·4	1·0	0·182	0·023 atm.
B.p. .	−93·5°	−100·9°	−119·°0	−129°	−138°	−153·6°	−167·0°	−176·5°

A. Ladenburg and C. Krügel gave —142·4° for the b.p.; P. A. Guye and G. Drouginine, —142°; H. Goldschmidt, —151·13°; F. A. Henglein and H. Krüger, —150·6°; M. W. Travers, —149·9°; P. A. Guye and G. Drouginine, —150°; and K. Adwentowsky, —150·2°. K. Olschewsky found the **vapour pressure** at —176·3° to be 18·2 mm., and at 166·8°, 138·3 mm.; W. Ramsay and M. W. Travers gave 760 mm. at —149·7°; and K. Adwentowsky, 23 mm. at —174·2°; 107 mm. at —164·3°; 441 mm. at —155·4°; and 760 mm. at —150·0°. F. A. Henglein and H. Krüger found the vap. press., p mm., to be:

	−199·57°	−192·82°	−171·8°	−164·0°	−161·1°	−155·9°	−152·8°	−150·5°	−148·4°
p .	0·0229	0·210	35·5	157·1	221·6	413·9	609·1	761·0	949·6
	Solid.				Liquid.				

The observed results can be represented by $\log p=10{\cdot}1466-867{\cdot}4T^{-1}$ for the solid, and by $\log p=8{\cdot}4440-681{\cdot}1T^{-1}$ for the liquid. The relation dp/pdT is relatively large, meaning that there is a relatively large change in the vap. press. for a relatively small change of temp. H. Goldschmidt found that the vap. press.,

p mm., of liquid nitric oxide can be represented by $\log p = 6{\cdot}92669 - 0{\cdot}016801T - 1{\cdot}75 \log T - 778{\cdot}13T^{-1}$; and for the solid, $\log p = 6{\cdot}92669 - 0{\cdot}005985T - 1{\cdot}75 \log T - 837{\cdot}42T^{-1}$. There is much association among the liquid molecules. K. Adwentowsky gave −167° for the f.p.; A. Ladenburg and C. Krügel, 150·0° for the **melting point**; H. Goldschmidt, −163·21°; A. Eucken and E. Karwat, −110°; F. A. Henglein and H. Krüger, −163·6°; and K. Adwentowsky, −160·6°. H. Goldschmidt gave for the **triple point** −163·21°; the vap. press. at the triple point is 172·2 mm.; the **latent heat of vaporization** of the liquid is 3199 cals. at −151·13°; 3230 cals. at −155°; 3289 cals. at −160°; and 3324 cals. at −163·21°; and for the solid, 3863 cals. at −163·21°; 3872 cals. at −165°; 3885 cals. at −168°; 3902 cals. at −173°; 3912 cals. at −177°; and 3923 cals. at −183°. F. A. Henglein and H. Krüger gave 3080 cals. for the latent heat of sublimation and 3980 cals. for the latent heat of vaporization at the m.p. The **latent heat of fusion** at the triple point is 539 cals. A. Eucken and E. Karwat gave 552 cals. per mol; and F. A. Henglein and H. Krüger, 900 cals. The value for **Trouton's constant** is 24·7, the high value indicating an association of the liquid. J. Thomsen gave for the **heat of formation** of nitric oxide from its elements −21·575 Cals.; and from nitrous oxide and oxygen, −24·83 Cals. M. Berthelot gave −21·6 Cals. for the heat of formation from its elements. J. C. Thomlinson calculated what he called the thermochemical eq. of the nitrogen in nitric oxide—*vide infra.* R. T. Birge and H. Sponer calculated for the heat of dissociation of NO, 7·9 volts or 182,000 cals. from the band spectrum, and 8·3 volts or 191,000 cals. from chemical data. H. C. Urey gave 45·3 for the **entropy** of the gas; and E. D. Eastman, 46·6 to 49·3.

P. L. Dulong gave 1·000302 for the **index of refraction** of nitric oxide for white light, and E. Mascart, 1·0002971 for Na-light. C. Cuthbertson and E. P. Metcalfe gave 1·0002939 for light of wave-length $589{\cdot}3\mu\mu$; and C. and M. Cuthbertson, $1{\cdot}0_{3}29776$ for $\lambda = 480{\cdot}0\mu\mu$; $1{\cdot}0_{3}29622$ for $\lambda = 1{\cdot}0_{3}5209$; $1{\cdot}0_{3}29474$ for $\lambda = 576{\cdot}9\mu\mu$; and $1{\cdot}0_{3}29306$ for $\lambda = 670{\cdot}8\mu\mu$. They represented their results by $\mu - 1 = 3{\cdot}5210 \times 10^{27}/(12216 \times 10^{27} - \lambda^{2})$. For liquid nitric oxide, G. D. Liveing and J. Dewar gave 1·329 for the C-line; 1·3305 for the D-line; 1·3345 for the F-line; 1·3278 for the G-line; 1·3257 for the Li-Line, $\lambda = 670{\cdot}55\mu\mu$; and 1·3368 for the In-line, $\lambda = 450{\cdot}96\mu\mu$. The refractive power by $(\mu - 1)/D = 0{\cdot}2634$; and $(\mu^{2} - 1)/(\mu^{2} + 2)D = 1{\cdot}163$. J. Koch measured the dispersion. J. Cabannes and J. Granier discussed the polarization of light diffused laterally in nitric oxide. C. V. Raman and K. S. Krishnan observed no appreciable double refraction at 2 atm. press.; and none for Kerr's constant. K. S. Krishnan found no magnetic double refraction with nitric oxide, showing that the paramagnetic molecules of the gas do not orient, as a whole, in the magnetic field. W. H. Bair, and H. O. Kneser studied the **spectrum** of nitric oxide. The **absorption spectrum** of nitric oxide gas was examined by D. Brewster,[4] W. A. Miller, E. Robiquet, F. Holweck, E. Luck, J. Moser, H. Sponser and J. J. Hopfield, H. Kreusler, E. C. Kemble and F. A. Jenkins, R. S. Mulliken and co-workers, F. A. Jenkins and co-workers, M. Guillery, and J. N. Lockyer. The **ultra-violet spectrum** was examined by H. Kreusler; the **ultra-red spectrum** by E. Warburg and G. Leithauser; and the spectrum of soln. by A. Kundt, and D. Gernez. R. T. Birge and H. Sponer studied the heat of ionization of the gas. E. P. Metcalfe studied the ionization of nitric oxide. C. A. Mackay gave 9·4 volts for the **ionizing potential**; A. L. Hughes and A. A. Dixon, 9·3 volts; H. D. Smyth and co-workers, 9 volts; and T. R. Hogness and E. G. Lunn, and R. A. Morton and R. W. Riding studied this subject. H. Sponer said that the excitation potentials of the levels of the nitric oxide molecule are 5·44 and 13·96 volts; hence the ionizing potential must exceed 14 volts. T. R. Hogness and E. G. Lunn studied the positive ray analysis and ionization of nitric oxide, and of mixtures of that gas with argon and helium. W. G. Palmer examined the effect of nitric oxide on the coherer in detecting electric waves.

S. Zimmermann found the specific **electrical conductivity** of water saturated with nitric oxide to be $36{\cdot}2 \times 10^{-5}$. He considers that the soln. in water is in part a chemical process: $4NO+2H_2O=2HNO_2+H_2N_2O_2$. L. M. M. Smith and C. R. Daily found that the **dielectric constant** is nearly the same as that of air, being 1·00044 at room temp., and 760 mm. press. The value of this constant is not appreciably affected by a magnetic field of 10,000 gauss. The subject was discussed by L. Pauling. Nitric oxide is paramagnetic. G. Quincke found the **magnetic susceptibility** at 16° and 760 mm. to be $+0·053\times10^{-6}$; T. Soné gave $48·8\times10^{-6}$; and J. Schulmeister gave $0·0278\times10^{-6}$ and $0·0232\times10^{-6}$ for a magnetizing force of 668·3; and $0·0496\times10^{-6}$ and $0·0437\times10^{-6}$ for a magnetizing force of 2721·8. E. Bauer and co-workers, and P. Weiss and A. Piccard measured the coeff. of magnetization of nitric oxide; while P. Debye and A. Huber inferred that, in harmony with P. Ehrenfest's view, the molecules of this paramagnetic gas do not become oriented under the influence of a magnetic field; and A. Huber observed no electrical polarization with gaseous, liquid, or solid nitric oxide. E. C. Fritts, J. H. van Vleck, and N. W. Taylor and G. N. Lewis discussed this subject. G. Gehlhoff studied the cathode fall of potential of the gas in a vacuum tube. M. F. Skinker and J. V. White investigated the motion of electrons in nitric oxide.

The solubility of nitric oxide in different solvents.—According to H. Davy, one vol. of *water* absorbs $\frac{1}{10}$th vol. of gas at ordinary temp.; W. Henry said that one vol. of water absorbs $\frac{1}{10}$th vol. of gas, and J. Dalton, $\frac{1}{27}$th vol. G. Hüfner found that 100 c.c. of water at 20° absorb 4·706 c.c. of nitric oxide at 760 mm. L. W. Winkler obtained for the coeff. of absorption, β, or the vol. of gas reduced to n.p. θ, absorbed by one vol. of liquid when the press. of the gas without the partial press. of the liquid is 760 mm.; the solubility, S, or the vol. of gas reduced to n.p. θ, absorbed by one vol. of liquid at 760 mm.; and w, the weight of gas in grams absorbed by 100 grms. of solvent when the total press. is 760 mm.

	0°	5°	10°	15°	20°	40°	60°	80°	100°
β .	0·0738	0·0646	0·0571	0·0515	0·0471	0·0351	0·0295	0·0270	0·0263
S .	0·0734	0·0641	0·0564	0·0506	0·0460	0·0325	0·0237	0·0144	0·0000
w .	0·00984	0·00860	0·00757	0·00680	0·00618	0·00440	0·00324	0·00199	0·00000

According to J. Dalton, 100 vols. of *nitric acid* of sp. gr. 1·3 absorb 20 vols. of nitric oxide. He added that the amount of nitric oxide absorbed is proportional to the conc. of the acid, HNO_3; very dil. acid absorbs scarcely any more nitric oxide than does pure water. A. V. Schaposchnikoff measured the coeff. of absorption of nitric oxide by nitric acid expressed in litres of gas per litre of acid of different conc., N, at 25°:

Conc. HNO_3 .	N-	0·4N-	0·2N-	0·1N-	0·075N-	0·05N-	0·025N-
NO . .	0·3209	0·1448	0·0753	0·03803	0·02852	0·0195	0·00981

An acid of sp. gr. 1·517 at 15°/4° absorbs 0·88 per cent. of nitric oxide so that the coeff. of absorption is 12·5. The speed of absorption varies with the conc. of the acid. C. A. Winkler obtained no absorption of nitric oxide by the hydrate of *sulphuric acid;* and M. Berthelot said that nitric oxide is very slightly soluble in conc. sulphuric acid. O. Lubarsch made some observations on this subject. E. Desbassayns de Richemont said that if the sulphuric acid contains a little ferrous sulphate, nitric oxide imparts to it a red colour; and if copper sulphate, a violet colour. In the latter case, W. Manchot found that the coloration is due to the formation of an easily dissociated *copper nitrosylsulphate*, $CuSO_4.NO$—*vide infra.* For the corresponding compound with ferrous sulphate, *vide infra.* G. Lunge found that 1 c.c. of sulphuric acid of sp. gr. 1·84 absorbs 0·035 c.c. of nitric oxide, and an acid of sp. gr. 1·50, 0·017 c.c.; and O. F. Tower, v vol. of nitric oxide at 760 mm. absorbed by one vol. of acid 18° and H_2SO_4 per cent.

.	98	90	80	70	60	50
v . . .	0·0227	0·0193	0·0117	0·0113	0·0118	0·0120

J. Priestley said that nitric oxide is very soluble in aq. soln. of *ferrous sulphate*, and of other ferrous salts; J. Dalton, that a soln. of ferrous sulphate of sp. gr. 1·081, containing one part by weight of ferrous sulphate to six parts of water absorbs 6 vols. of nitric oxide. E. Péligot showed that 2 mols of the ferrous salt absorb one mol of nitric oxide. If v represents the number of litres of soln. containing one mol of ferrous sulphate ; and S number of litres of nitric oxide absorbed, then V. Kohlschütter found :

v . .	1·2	1·8	2·4	4·82	7·2	12·0	18·6	36·0
S . .	1·47	2·01	2·55	4·40	5·52	5·36	8·01	10·40

J. Gay showed that the amount of gas absorbed is proportional to the amount of iron present irrespective of the acid, or the conc. of the soln. The absorption is also dependent on the temp. and press. Thus, between 0° and 10°, about 2 mols of nitric oxide are absorbed per gram-atom of iron ; between 10° and 15°, in agreement with E. Péligot, one mol of nitric oxide for 2 gram-atoms of iron ; and at 25°, only one mol of nitric oxide per 2·5–3 gram-atoms of iron. The sp. gr. of the soln. is greater after the absorption of nitric oxide than it was before. The soln. are decomposed by heat, and at 100°, all the nitric oxide is expelled. The cooling or evap. of the soln. in an atm. of nitric oxide yields black crystals which contain very little nitric oxide. L. Moser and R. Herzner found that the most efficient soln. for analytical work contains 15 per cent. by wt. of anhydrous ferrous sulphate, 15 per cent. of 64 per cent. sulphuric acid, and 70 per cent. of water. S. Zimmermann found that soln. after the absorption of nitric oxide have a smaller conductivity than before, and the complex ion containing nitric oxide has a smaller transport number than the iron-ion. F. L. Usher found that owing to chemical interaction, neither the f.p. of the soln. nor the press. of the nitric oxide remained constant. The nitric oxide is reduced by soln. of ferrous sulphate so that the vol. of gas absorbed gradually increases with time. This interferes with the exact measurement of the solubility. G. von Hüfner gave for the coeff. of absorption, β, of 205·69 c.c. of a soln. containing w gram-atoms of iron, at 20·09° :

w . .	0·0221	0·0296	0·0409	10·0513	0·0663	0·099
β . .	0·06067	0·06505	0·06684	0·07981	0·08059	0·11661

He argued that the nitric oxide must be in some way attached to the metal because the amount of gas absorbed increases with the conc. of the salt soln. ; and he added that the connection is so " loose " that within certain limits of press., the absorption of the gas is in accord with Henry's law. W. Manchot and K. Zechentmayer showed that the absorption of nitric oxide by a ferrous salt results from the formation of a chemical compound containing Fe and NO in the proportion 1 : 1. Under all conditions, therefore, the limit of absorption is reached when 1 mol. of nitric oxide has been absorbed for each ferrous atom present, and corresponds with the conversion of Fe'' into Fe'''. The formation of the compound is a reversible reaction ; the degree of dissociation varies with the ferrous salt, but is dependent also on the press., temp., conc. of the ferrous salt, presence of indifferent solutes, and nature of the solvent, to an extent which is in agreement with the laws of chemical dissociation. W. Manchot and co-workers regarded the product of the reaction as **ferrous nitrosylsulphate,** $FeSO_4.NO$, which was isolated in red leaflets by W. Manchot and F. Huttner, W. Manchot, and I. Bellucci. J. Dalton said that a soln. of *ferric* sulphate does not absorb nitric oxide—presumably to any marked extent. W. Manchot and E. Linckh found that ferrous selenate behaves like ferrous sulphate in absorbing nitric oxide, and a similar ring test may be made with ferrous selenate and conc. selenic acid. The combination is similar to that in the case of ferrous sulphate, giving an equilibrium constant on the assumption that the combining ratio is 1 : 1. The equilibrium constant, 162, is rather smaller than that obtained with ferrous sulphate. Crystalline **ferrous nitrosylselenate,** $FeSeO_4.NO.4H_2O$, may be prepared by saturating a conc. aq. soln. of ferrous selenate, $FeSeO_4.5H_2O$, with nitric oxide in the presence of a little conc. selenic acid. On adding a large excess of absolute alcohol, also sat. with nitric oxide, with cooling in a freezing mixture, brownish-black crystals appear after some hours. The crystals are unstable, losing nitric oxide when kept in air, but the composition is that indicated above. W. Manchot found that a soln. of ferric sulphate in 90 per cent. sulphuric acid forms **ferric nitrosylsulphate,** $Fe_2(SO_4)_3.NO$. G. Hüfner also found that the coeff. of absorption for 205·69 c.c. of a soln. of *cobalt sulphate* with 0·0598 gram-atom of cobalt is 0·09146 at 20·09°; and for 205·69 c.c. of a soln. of *nickel sulphate* with 0·0506 gram-atom of nickel, it is 0·08311. For soln. of the same conc., F. L. Usher gave 0·048 at 20° with nickel sulphate, and 0·0245 for a soln. sat. at 20°; and for a soln. of cobalt sulphate sat. at 20°, 0·0288. Thus, while G. Hüfner found the coeff. of absorption of nitric oxide in cobalt and nickel sulphates to be high, F. L. Usher claimed that the presence of these salts diminishes the solubility of nitric oxide in water. L. Moser and R. Herzner studied the solubility from the point of view of analysis.

V. Kohlschütter and M. Kutscheroff found that v litres of water containing a mol of *ferrous chloride* absorb S litres of nitric oxide; thus:

v . . .	2·5	5·18	10·35	20·7	51·8
S . . .	3·30	4·83	6·56	8·32	11·89

The solubility of nitric oxide in presence of 10 per cent. hydrochloric acid is rather less than in an aq. soln. of the same conc., as W. Manchot and K. Zechtenmayer have observed, but with 30 per cent. hydrochloric acid, the solubility is approximately doubled. They also found that a soln. of a mol of ferrous chloride in 10·37 litres sat. with sodium chloride absorbed 6·549 litres of nitric oxide; and when the sodium chloride is replaced by ammonium chloride, 6·549 litres of nitric oxide are absorbed. According to V. Thomas, anhydrous *ferric chloride* absorbs nitric oxide at the ordinary temp., forming a brown complex **ferric nitrosylhexachloride,** $2FeCl_3.NO$; and at 60°, **ferric nitrosyldodecachloride,** $4FeCl_3.NO$. The same compounds are formed when nitric oxide is passed into soln. of ferric chloride. At the temp. of sublimation, ferric chloride is reduced by nitric oxide. These two salts are very hygroscopic, and could not be crystallized; they give off nitric oxide when in contact with water; and when heated in air, form ferric oxide. When nitric oxide is passed into ether sat. with ferric chloride, and the soln. evaporated over sulphuric acid, black needles of **dihydrated ferrous nitrosyldichloride,** $FeCl_2(NO).2H_2O$, are formed; and if the crystallization occurs at 60°, yellow crystals of anhydrous **ferrous nitrosyldichloride,** $FeCl_2(NO)$, are produced. This compound dissolves completely in water, without evolution of gas, and yields a pale yellow solution, the colour of which deepens when heated. On addition of alkalies out of contact with air, ferrous oxide is precipitated, but no gas is evolved. The solution gives other reactions of ferrous salts. V. Thomas found that these three nitrosyl compounds have no appreciable dissociation press. at ordinary temp., either in vacuo, or in a current of a dry inert gas. Water dissolves ferrous nitrosyldichloride without an evolution of gas, and no gas is evolved if the other two compounds are added to a large proportion of water; but if water is allowed to drop on the solid compounds, gas is liberated in large quantity. Potassium hydroxide or ammonia behaves similarly with all three compounds, and produces a greyish-white precipitate which rapidly becomes bluish-green and, finally, black. There is no liberation of gas, and the liquid contains neither a nitrate nor a nitrite, nor ammonia. When the black precipitate, produced by alkalis in solutions of the solid compounds, is placed in a vacuum, it gives off a considerable quantity of almost pure nitrogen. If a soln. of the nitrosyl dichloride is precipitated with silver nitrate, there seem to be indications of the formation of silver hyponitrite; but this supposition could not be confirmed, and the phenomena are not shown by the other two compounds. Nitric oxide is only very slowly absorbed by solutions of the ferrous nitrosyl chlorides, and seems to act as an oxidizing agent. W. Manchot and F. Huttner studied the equilibrium conditions of the reaction $FeCl_2+NO \rightleftharpoons FeCl_2.NO$, but I. Bellucci could not confirm the existence of ferrous nitrosyldichloride, although he did obtain W. Manchot's **ferrous nitrosylhydrophosphate,** $Fe(NO)(HPO_4)$. W. Manchot also prepared **copper nitrosylsulphate,** $Cu(NO)SO_4$; **copper nitrosylchloride,** $Cu(NO)Cl_2$; and **copper nitrosylbromide,** $Cu(NO)Br_2$; but the nitrosyl salts could not be obtained with copper fluoride, nitrate, acetate, tartrate, formate, and glycollate. V. Thomas found that at 10° soln. of *ferrous bromide* absorb nitric oxide and appear to form **ferrous dinitrosylhexabromide,** $3FeBr_2.2NO$; and at 15°–16°, **ferrous nitrosyltetrabromide,** $2FeBr_2.NO$. These results agree with those of J. Gay obtained with ferrous sulphate and chloride. W. Manchot studied the equilibrium conditions of the reaction $FeBr_2+NO \rightleftharpoons FeBr_2.NO$; but I. Bellucci doubts the existence of this nitrosylbromide. With *ferric bromide* the reduction occurs more readily than with ferric chloride, and the resulting ferrous bromide absorbs nitric oxide as just indicated. W. Manchot and E. Linckh, and H. I. Schlesinger and A. Salathe measured the absorption spectra of the nitrosyl copper and ferrous sulphates. W. Manchot and E. Linckh found that the absorption spectra of the nitrosyl compound in soln. of varying concentration are independent of the Cl'-, SO_4-, and SeO_4-anions, and are determined by the $(FeNO)'$-cation. The spectra of the green soln. of the ferrous nitrosyl chloride in alcohols, esters, or hydrochloric acid are quite similar, indicating that hydrogen chloride may replace alcohol or ester in the complex which causes the colour. The spectrum of red soln. of the ferrous nitrosyl sulphate in conc. sulphuric acid, or of the chloride in pyridine denotes that the colouring complex has a different structure. Soln. of cupric nitrosyl salts in conc. sulphuric acid, alcohol, or ethyl acetate were found by W. Manchot and E. Linckh to have closely similar absorption spectra resembling the green type of ferrous nitrosyl salts; and the colour appears to be due to the CuX_2NO complex. The red ferrous nitrosyl salts have no counterpart among the copper salts; nor do brown copper salts analogous to brown ferrous nitrosyl salts exist. H. I. Schlesinger and A. Salathe, and L. Cambi and L. Szego also studied the absorption spectra of soln. of the nitrosyl ferrous and copper sulphates. G. Hüfner found that at 20·09°, 205·69 c.c. of a soln. of *manganous chloride* containing 0·0697 grm. of manganese, had a coeff. of absorption 0·06111, and the solubility increased with increasing press. F. L. Usher found a soln. of this salt sat. at 20° had a coeff. of absorption of 0·0082. V. Kohlschütter and M. Kutscheroff found that at 23°, 3·25, 6·50, and 26·00 litres of soln. containing a mol of *ferrous nitrate,* absorb respectively 2·77, 4·16, and 6·61 litres of nitric oxide. They also obtained with 0·231, 0·277, and 0·371 litre of a soln. containing a mol of *cupric chloride,* an absorption of 0·120, 0·098, and 0·052 litre respectively of nitric oxide; with v litres of conc. hydrochloric acid containing a mol of cupric chloride, S litres of gas were absorbed.

v .	0·389	0·840	1·230	2·462	7·499	12·500	18·750	28·650
S .	0·801	2·838	3·426	3·989	3·931	3·606	3·153	1·976

They also tried soln. of cupric chloride in acetic acid, formic acid, acetone, and methyl and ethyl alcohols. With 0·37, 0·62, and 0·925 litre of soln. with a mol of *cupric bromide,* 0·515, 0·120, and 0·000 litre of nitric oxide were respectively absorbed. They also tried soln. of cupric bromide in ethyl alcohol. E. Péligot found that nitric oxide is absorbed by aq. soln. of *stannous salts* (*vide infra*) and *chromous salts.* According to G. Chesneau, a soln. of *chromous chloride* absorbs nitric oxide in the ratio $CrCl_2 : NO = 3 : 1$, and the blue liquid becomes dark red. When heated, the nitric oxide is not expelled as in the case of ferrous salts, but the liquid becomes greenish-brown, and the nitric oxide is reduced to ammonia or hydroxylamine. The action of nitric oxide on soln. of chromous salts was also studied by V. Kohlschütter, and J. Sand and O. Burger.

Nitrosyl compounds of copper, manganese, iron, cobalt, nickel, and palladium are also known. W. Manchot and H. Schmid described the preparation of **potassium manganese nitrosylcyanide,** K_3MnCy_5NO, from the action of nitric oxide on a soln. of potassium cyanide and manganese chloride or acetate. W. Manchot and A. Waldmüller prepared **palladium dinitrosyldichloride,** $PdCl_2(NO)_2$, by the action of nitric oxide on a soln. of palladous chloride; with palladous sulphate, **palladium dinitrosylsulphate,** $PdSO_4(NO)_2$, is formed; and with palladium nitrate, palladium nitrite, $Pd(NO_2)_2$, is formed.

R. Bunsen found that S vols. of nitric oxide reduced to n.p.t. are absorbed by one vol. of absolute *ethyl alcohol* at 750 mm.,

	0°	5°	10°	15°	20°	24°
S . .	0·31606	0·29985	0·28609	0·27478	0·26592	0·26060

and L. Carius represented the results by $S=0·21606-0·003487\theta+0·000049\theta^2$ between 0° and 25°, and 760 mm. L. H. Friedburg found that nitric oxide is abundantly absorbed by *carbon disulphide.* Alkaline soln. of *pyrogallol* were shown by W. Lapraik, and G. Lechartier, to absorb nitric oxide, and by C. Oppenheimer to reduce it to nitrous oxide. R. A. Smith said that *charcoal* absorbs 12·66 times its vol. of nitric oxide; and C. Montemartini found that 4·441 grms. of *palladium* black absorbed 163·6 c.c. of nitric oxide in 2 days.

The chemical properties of nitric oxide.—Nitric oxide is not combustible, and it supports the combustion of a few substances, but not that of a candle. Nitric oxide is irrespirable since, in the presence of air, it forms brown fumes of nitrogen peroxide. L. Hermann[5] said that oxygenated blood is darkened when shaken with nitric oxide, and it seems to form a *nitrosylhæmaglobin.* W. Manchot discussed the compounds formed by nitric oxide with blood. F. Hatton showed that the bacteria which are connected with the putrefaction of meat extracts develop quite well in an atm. of nitric oxide.

The analyses of H. Davy, and J. L. Gay Lussac and L. J. Thénard show that nitric oxide has the empirical composition NO. This formula agrees with the physical properties of the gas. Oxygen is bivalent, hence the nitrogen in nitric oxide also behaves as a bivalent element: $O{=}N$; but nitrogen is usually ter- or quinque-valent, so that nitric oxide is usually considered to be an unsaturated compound. No evidence of the existence of $O{=}N{-}N{=}O$ has been observed. C. Weltzien considers that the radicle NO is sometimes univalent, and sometimes bivalent. J. C. Thomlinson's calculations of the thermochemical eq. of nitrogen in nitric oxide favoured the assumption that the oxygen is quinquevalent. E. Müller discussed this subject; and E. C. Stoner, and C. D. Niven, the electronic structure.

Nitric oxide is one of the most stable oxides of nitrogen. J. L. Gay Lussac[6] observed that when nitric oxide is passed through a red-hot tube, which contains platinum wire, it is decomposed into nitrogen and nitrogen peroxide; but W. R. E. Hodgkinson and F. K. S. Lowndes observed no decomposition when a platinum wire is electrically heated in an atm. of nitric oxide. M. Berthelot found that the gas begins to decompose when heated in a sealed tube at 520°, and in half an hour, about one-fourth of the gas is decomposed into nitrogen, nitrous oxide, and nitrogen tri- and per-oxides. K. Jellinek noted that decomposition can be detected at 689°, and that moisture has no influence on the reaction. For the equilibrium conditions, *vide supra,* the fixation of nitrogen. F. Emich, and C. Langer and V. Meyer noted that the gas is completely decomposed at about 1690°; at 700°, about 0·5 per cent. is decomposed; at 900°, one per cent.; and at 1200°, 60 per cent. The dissociation of nitric oxide: $2NO\rightleftharpoons N_2+O_2$, with rise of temp. has been discussed in connection with the fixation of nitrogen. E. Briner and N. Boubnoff studied the reaction over the range of press. from 50 to 700 atm., and over the temp. range from −90° to 300°. Nitrogen, nitric and nitrous oxides, and nitrogen trioxide and peroxide were among the products. It is inferred that the main reactions are: $2NO \rightleftharpoons N_2+O_2$; and $4NO=2N_2O+O_2$. The latter predominates. The other nitrogen oxides are supposed to be formed by the secondary action of oxygen on untransformed nitric oxide. The reaction was studied by W. Muthmann and H. Hofer, C. Meiner, W. Nernst, J. Brode, and P. A. Guye and F. Schneider—*vide supra.* E. Calberla said that at a bright red-heat, all the gas is decomposed in the presence of silver, but F. Emich could not verify this statement. While the reaction: $2NO=N_2+O_2$ is bimolecular in the gas phase, C. N. Hinshelwood and T. E. Green found that it is unimolecular on the surface of a heated platinum wire between 273° and 1531°. It is not influenced by nitrogen, but is retarded by oxygen. Thus, the velocity constant falls from $k=0{\cdot}0023$ with a 13 per cent. decomposition, to 0·0007 with 40 per cent. decomposition. M. Berthelot found that if mercury fulminate be exploded in nitric oxide, the gas is decomposed. J. Priestley observed that the gas is decomposed by the passage of electric sparks, forming, according to M. Berthelot, nitrogen, oxygen, and a trace of nitrous oxide. The decomposition of nitric oxide by electric sparks was noted by H. Buff and A. W. Hofmann, W. R. Grove, and T. Andrews and P. G. Tait. The decomposition of the gas by radiations of short wave-length was noted by E. Warburg and E. Regener. C. B. Bazzoni and A. T. Waldie said that at press. ranging from 0·1 mm. to 180 mm., nitric oxide is not dissociated either by heat radiation or by ultra-violet light; but D. Berthelot and H. Gaudechon observed that it is decomposed into nitrogen and oxygen by the light from a mercury quartz lamp, and that the oxygen unites with the remaining nitric oxide to form higher oxides. According to E. Briner and A. Wroczynsky, if nitric oxide be allowed to remain at a high press. in a sealed tube, drops of a blue liquid are first noticed at 28 atm. press.; $6NO=2N_2O_3+N_2$. E. Briner, and co-workers observed nitric oxide under prolonged compression decomposes, yielding a blue liquid which consists of a mixture of nitrous oxide and nitrous anhydride. Nitric oxide decomposes to give nitrous oxide and oxygen, the oxygen reacts with unchanged nitric oxide, yielding the peroxide, which in turn may react with nitric oxide to form the trioxide. The decomposition is very rapid at 700 atm. At lower press., the reaction is retarded by corrosion of the glass vessels by nitrogen peroxide. Freshly prepared and condensed nitric oxide is only very faintly blue in colour. Multiple liquefaction does not affect purification, since the blue colour gradually increases in intensity. Liquid nitric oxide is probably colourless and the blue tint is due to nitrous anhydride. E. Briner and co-workers studied the decomposition of nitric oxide at 700 atm. press.

C. L. Berthollet contradicted the statement of A. F. de Fourcroy, and T. Thomson that when a mixture of equal vols. of nitric oxide and **hydrogen** is passed through a red-hot tube, a detonation occurs. D. Waldie found that a mixture of nitric oxide and hydrogen burns with a white flame in air, without explosion, forming nitrogen peroxide; the hydrogen is said to be oxidized by the atm. oxygen, since a hydrogen flame is extinguished in nitric oxide. C. von Than determined nitric oxide by exploding a mixture of it with hydrogen by an electric spark: $2NO+2H_2=N_2+2H_2O$. H. Davy obtained no explosion by sparking a mixture of equal vols. of hydrogen and nitric oxide. S. Cooke said that it requires intense and long sparks to explode the 1 : 1 or 2 : 1 mixture of nitric oxide and hydrogen, while a mixture with more than 3 : 5 of hydrogen can no longer be exploded. C. von Than found that the reaction $2NO+2H_2=N_2+2H_2O$ can be completed by sparking the mixed gases. C. N. Hinshelwood and T. E. Green found that the homogeneous reaction between nitric oxide and hydrogen between 727° and 827° is termolecular, proceeding according to the ultimate reaction $2NO+2H_2=N_2+2H_2O$ at 826°, the value of K in $d[NO]/dt=K[NO]^2[H_2]$, ranges between $1{\cdot}08\times10^{-7}$ and $1{\cdot}60\times10^{-7}$ for considerable variations in the concentrations of hydrogen and nitric oxide expressed in mm. press., and the time in seconds. There is a small surface action which becomes more marked at lower press. The heat of activation is 44,000 cals. M. Faraday observed that a platinum plate in the mixture gradually induces combination. G. von Knorre and K. Arndt determined the nitric oxide in a gas from the contraction which occurs after passing a mixture of it with hydrogen over heated platinum sponge: $2NO+2H_2=N_2+2H_2O$. According to S. Cooke, a little hydrogen occluded in platinum reduces nitric oxide to nitrogen and nitrous oxide, but with more hydrogen, hydroxylamine, and ammonia are formed. L. Duparc and co-workers found that nitric oxide is reduced by hydrogen in the presence of platinum or rhodium to ammonia, while nitrous oxide always yields nitrogen. E. Ludwig and T. Hein found that with nascent hydrogen from tin and hydrochloric acid, hydroxylamine is formed (*q.v.*); J. H. Gladstone and A. Tribe, that with a copper-zinc couple, ammonia is produced; and R. S. Felgate, that nitric oxide is reduced to nitrogen by passing the gas through water with nickel reduced from the hydroxide by hydrogen. The nickel is at some time oxidized. A colloidal soln. of nickel does not produce the same result. P. Sabatier and J. B. Senderens observed no reduction when palladium sat. with hydrogen is surrounded by nitric oxide in the cold, but at 200°, the metal glows, forming water, ammonia, and a little nitrogen; nickel and copper at 180° also act as catalysts in this reaction; P. Neogi and B. B. Adhicary said that the reaction with nickel commences at 300° and then proceeds at 120° almost quantitatively; they also found that the reduction of nitric oxide in the presence of 3 times its vol. of hydrogen proceeds almost quantitatively in the presence of finely divided tin, iron, or zinc, whilst magnesium, mercury, and aluminium are inactive. Antimony and bismuth when freshly reduced from their oxides also exert a catalytic action. Gold, silver, or lead in the form of foil are almost inactive, but the freshly reduced metals in the form of powder cause the production of large quantities of ammonia. Gold acts best at 335°–345°; and silver at 430°. E. Briner and co-workers found that platinum with the alkaline earths as promoters was the most advantageous catalyst tried; and they found a parallelism between the catalytic efficiency and the electronic emission. P. A. Guye and F. Schneider represented the reduction of nitric oxide by nickel as the result of two consecutive reactions, one giving ammonia: $2NO+5H_2=2NH_3+2H_2O$, and the other nitrogen: $2NO+H_2=N_2+H_2O$. No nitrous oxide is produced. A temp. of 250°–300° is most suitable for the ammonia-reaction when 70 per cent. of the nitric oxide is transformed with ammonia. H. Gall and W. Manchot found that the NO-group of sodium nitroprusside was not reduced by hydrogen to the NH_3-group with aq. soln. and spongy platinum as catalyst. H. Moissan found that when **calcium hydride** is heated to dull redness in an atm. of nitric oxide the mass becomes incandescent and much ammonia is formed—*vide supra*, the formation of ammonia.

The early workers observed that when nitric oxide is brought in contact with **air** or **oxygen,** ruddy fumes of nitrogen peroxide are produced $2NO+O_2=2NO_2$. Numerous lecture experiments have been devised for illustrating this reaction—*e.g.* by G. Bruylants, etc.—*vide infra*, nitrogen peroxide, and *vide supra*, nitrosonitrogen trioxide for the action of oxygen on nitric oxide at very low temp. R. Pictet found that the reaction occurs very slowly at —80°, but at —120°, there is no reaction. H. B. Baker showed that if the gases be thoroughly dried, nitric oxide does not react with oxygen, although F. Emich did not succeed in the demonstration. According to J. L. Gay Lussac, and E. Péligot, in the cold, and in the absence of water and bases, nitrogen peroxide is the chief product; while P. L. Dulong, and J. J. Berzelius hold that nitrogen trioxide is formed. M. Berthelot said that in the presence of an excess of oxygen, nitrogen trioxide is first formed, and afterwards nitrogen peroxide is produced. This was confirmed by F. Raschig, who also suggested, without proof, that higher oxides are formed. He also stated that nitric oxide and oxygen unite in the fraction of a second to form nitrous anhydride: $(n+1)O_2+4NO \rightarrow nO_2+2N_2O_3$, and the anhydride, N_2O_3, then slowly oxidizes to the peroxide, N_2O_4. G. Lunge and co-workers claimed that with an excess of oxygen, nitrogen peroxide is first formed; and if nitric oxide be in excess, both nitrogen tri- and peroxides are formed, and at —21°, the nitrogen peroxide unites with nitric oxide, forming nitrogen trioxide (*q.v.*). If water is present, and the oxygen is in excess, only nitric acid is formed, and in the presence of sulphuric acid, nitrosylsulphonic acid is produced, but no nitrogen peroxide or nitric acid is formed. G. Lunge and E. Berl said that the reaction: $2NO+O_2=2NO_2$ is termolecular. The data were found by G. W. Todd to give sensibly constant values for the velocity coeff. at 20° with oxygen and nitric oxide; but with air, higher values are found in the earlier stages of the reaction. This is ascribed to the time required for mixing the reacting gases. F. Haber and W. Holwech, and F. Förster and A. Blich found that the oxidation of nitric oxide to nitrogen peroxide is a comparatively slow reaction, and the latter obtained a small negative velocity coeff. between 0° and 100°. They therefore assumed that a direct addition of oxygen to form a complex oxide occurs : $NO+O_2=NO.O_2$, which then reacts with a second molecule of nitric oxide to form nitrogen peroxide: $NO.O_2+NO=2NO_2$. The first reaction is reversible and the equilibrium state with a rise of temp. favours the dissociation of the complex oxide. The smaller conc. of the complex oxide at the higher temp. more than counteracts the increased velocity between the complex oxide and nitric oxide. The subject was discussed by J. Wiswald.

L. Francesconi and N. Sciacca showed that at the temp. of liquid air, the action of oxygen on nitric oxide results in the formation of nitrogen peroxide, whatever proportions of nitric oxide and oxygen be taken, provided the temp. be below —110°; only above —100° is nitrogen trioxide transformed by oxygen to nitrogen peroxide; and nitrogen peroxide is reduced by nitric oxide to nitrogen trioxide at temp. below —150°. According to A. Sanfourche, the first stage in the oxidation of nitric oxide: $4NO+O_2=2N_2O_3$, is practically instantaneous and independent of temp. between —50° and 525°. The second stage is a reversible process: $2N_2O_3+O_2\rightleftharpoons4NO_2$. The equilibrium is displaced from left to right up to 200°, but tends more and more from right to left as the temp. rises from 200° to 525°. The velocity of the oxidation has been measured by M. Bodenstein, the reaction is termolecular, and a rise of temp. lessens the speed of the reaction $dx/dt=kC_0C_1$, where C_1 denotes the conc. of nitric oxide, and C_0, that of oxygen. E. Briner and E. Fridöri said that over the interval of temp. 0°–60°, lowering the temp. 10° raises the velocity 10–20 per cent. The speed of the reaction was also studied by M. Trautz, E. Briner and co-workers, S. Dushman, and G. B. Taylor and co-workers. E. Wourtzel found that the reaction is of the third order, with a velocity—$dx/dt=kx^2p$, where x denotes the partial press. of the nitric oxide; and p, that of the oxygen. E. Briner and co-workers found that the third order of reaction becomes of the second order when a large excess of oxygen is present. A little nitrogen trioxide is formed: $NO+NO_2=N_2O_3$. According to A. Sanfourche, in the presence of water, nitric oxide is oxidized to nitrogen trioxide and not to the peroxide, the trioxide then being decomposed by the water, giving nitric acid and a partial regeneration of nitric oxide. In the presence of nitric acid (sp. gr. 1·5), however, the nitrogen trioxide is oxidized with the formation of the peroxide and water, according to the equation $2HNO_3+N_2O_3=H_2O+2N_2O_4$. This oxidation is first noticeable with nitric acid (sp. gr. 1·3), which has a concentration of approximately 50 per cent. but is not complete, and progresses further as the concentration of the nitric acid used is increased. E. Briner concluded that although water favours the reaction, its presence is not an essential condition for the reaction between oxygen and nitric oxide.

In 1846, I. T. Jullion patented the use of platinized asbestos for the oxidation of nitric oxide to nitric acid. C. L. Burdick found that between 0° and 100°, the oxidation of nitric oxide by oxygen is not catalyzed by ordinary porous materials —glass, pumice, or pumice impregnated with tungstic oxide—but with other agents—nickel, cobalt, or nickel, cobalt, or manganese oxides, platinized pumice or asbestos, coke, or charcoal—the reaction is accelerated. In the case of the highly absorptive varieties of charcoal, the reaction may be accelerated 500 times. The presence of water vapour in the gaseous mixtures greatly decreases the activity of the charcoal catalysts. An increase of temp. above the point at which the aq. vap. condenses counteracts this effect to some extent. The temp. coeff. of the velocity of reaction for both the catalyzed and uncatalyzed change is generally negative. In the presence of water vapour, the temp. coeff. of the catalyzed reaction is positive. This is probably due to the decreased absorption of water by the catalyst at elevated temp. The velocity of reaction increases greatly as the temp. is lowered, particularly at very low temp. The temp. coeff. of the velocity constant (defined as the ratio of the velocity constants at two temp. differing by 10°) decreases from 0·96 at 70° to 0·85 at —180°, in contrast to the values of 2–3 for ordinary reactions. The oxidation of nitric oxide is greatly facilitated by the cooling of the gases, particularly if the cooling takes place immediately the gases leave the arc. R. L. Hasche found that the reaction is accelerated by moisture, and the decrease in velocity observed when the interior of a glass vessel is coated with paraffin is attributed to a decreased film of moisture on the surface. The speed of oxidation can be reduced 30 per cent. by excluding water. There is a period of induction which is a function of the press. and of the humidity of the gas. The moisture is supposed to act as a catalytic agent: $NO+H_2O=NO.H_2O$; $NO.H_2O+NO=(NO)_2.H_2O$; and $(NO)_2.H_2O+O_2=N_2O_4(\rightleftharpoons 2NO_2)+H_2O$. The presence of sulphur dioxide, or of nitrogen peroxide, had no perceptible influence. M. Latshaw and W. A. Patrick studied the rate of oxidation of nitric oxide in an apparatus in which the changes of press. of the manometer were recorded on a photographic film mounted on the drum of a kymograph. R. L. Hasche observed that a period of induction occupying about 10 seconds occurs when the initial pressure of the mixed gases is below 14 mm. of mercury. J. L. Gay Lussac observed that a mixture of one vol. of oxygen with not more than four vols. of nitric oxide, in the presence of potash-lye, forms potassium nitrate; and T. Schlösing showed that if oxygen be in excess, the nitric oxide is converted completely into the nitrate. F. Fischer said that some nitrite is formed. W. A. Lampadius reported that if nitric oxide be added to oxygen standing over water at about 52° some nitric acid is formed. A. K. Brewer and F. Daniels showed that when nitric oxide is oxidized between oppositely charged electrodes a current of electricity passed through the gases. The current is of the order of 10^{-14} amperes for the oxidation of 50 c.c. of nitric oxide per minute reacting in a field of 450 volts per cm. This corresponds with about one ion for every million molecules reacting. The current is directly proportional to the voltage and to the number of molecules reacting. No evidence of a saturation current could be detected. A. Mandl and F. Russ found that the reaction with a mixture of 2 vols. of nitric oxide and one vol. of oxygen does not always go to an end. In some cases, only 97 per cent. of the nitric oxide is oxidized. Thus, electrolytic oxygen is said to be more active after passage over heated palladium. The retardation is possibly due to traces of hydrogen dioxide or ozone in the oxygen either directly or by the destruction of some catalyst necessary for the reaction. W. Holwech denied the phenomenon, and said that the speed of the reaction is the same with oxygen from all sources. For the reversibility of this reaction at high temp., *vide infra*, nitrogen peroxide. G. Kornfeld observed that the reaction with the two paramagnetic gases: $2NO+O_2=N_2O_4$, is slightly accelerated by a magnetic field.

A. Reis and O. Waldbauer obtained steady flames from mixtures of methane, nitric oxide, and oxygen; and the flames could be readily separated into two cones. If small percentages of nitric oxide are present, the gases from the inner cone contain ammonia, hydrogen cyanide, and acetylene. The proportion of hydrogen cyanide decreases with increasing height, while the proportion of ammonia rises to a maximum, and then falls. This shows that the ammonia is derived from the hydrogen cyanide. If a large proportion of nitric oxide is present, the inner cone has the appearance of substances burning in nitrogen peroxide. Here 90 per cent. of the nitrogen peroxide is transformed into nitric oxide, which then passes out of the inner cone unchanged; from 25–33 per cent. of the methane also escapes from the inner cone unchanged. The hydrogen is almost wholly oxidized, but the carbon monoxide is only slightly oxidized. Some formaldehyde is present in the gases between the two zones. The gases between the zones contain 40 per cent. of nitric oxide mixed with combustible gases and vapours. In this zone, too, the nitric oxide is only slightly decomposed, but the methane is unchanged ; and the conc. of the hydrogen increases upwards while the conc. of the carbon monoxide decreases. When the gases between the two zones contain sufficient oxygen, a new cone appears between the inner and outer cones, and in the middle cone, the combustible gases are burnt at the expense of the nitric oxide. A. Pinkus observed no sign of ionization in the oxidation of nitric oxide by oxygen ; but A. Pinkus and M. de Schulthess found that the reaction between conc. **ozone** and nitric oxide takes place with the evolution of light, and has the character of an explosion when the quantity of ozone present is small. A. K. Brewer noted ionization in the oxidation of nitric oxide by oxygen at 50° and 385°, and by ozone at 50°.

According to J. L. Gay Lussac, if a mixture of **water** vapour, oxygen, and nitric oxide be passed through a red-hot tube, containing some platinum wire, nitric acid is formed. According to P. Villard, at 0° and 10 atm. press., or at 12° and 43 atm. press., an unstable *hydrated nitric oxide* is formed. W. J. Russell and W. Lapraik found that if nitric oxide and water be heated for a long time in a sealed tube, nitrous acid, nitrous oxide, and nitrogen are formed. S. Cooke said that nitric oxide is gradually altered by prolonged contact with water, and if platinum be also present, there is a large contraction, and nitrous acid with some nitrogen and nitrous oxide are formed ; without the platinum, the reaction occupies nine months at ordinary temp. ; but at a higher temp., the reaction is faster. According to L. Moser, E. J. Joss, and S. Zimmermann, nitric oxide cannot be preserved over water without change, partly owing to the dissolved oxygen, and partly owing to hydrolysis : $4NO+2H_2O=2HNO_2+H_2N_2O_2$; as A. Hantzsch and L. Kauffmann have shown, the hyponitrous acid produces nitrous oxide and ammonium nitrite, which further decomposes into nitrogen. This product increases slowly with the length of time the gas remains over water. The moist gas can, however, be kept indefinitely over mercury without change. R. S. Felgate found that the reaction with hot water is accelerated by nickel with the production of nickel oxide and nitrogen. For the solubility, *vide supra.* The aq. soln. does not redden litmus. J. L. Gay Lussac, and W. J. Russell and W. Lapraik observed that when in contact with a conc. aq. soln. of **potassium hydroxide,** potassium nitrite and nitrous oxide are formed : $4NO+2KOH=N_2O+2KNO_2+H_2O$; and S. Cooke found that the reaction is speedier if platinum be present. G. Barr, and S. Cooke said that some nitrogen is also formed. F. Emich noted that at 112°–113°, solid potassium hydroxide reacts quickly with nitric oxide. O. Baudisch and G. Klinger represented the reaction : $4NO+O_2+4KOH=4KNO_2+2H_2O$, and utilized it in removing nitric oxide from gases for analysis. F. L. Usher also found that the gas is decomposed by potash-lye so that the solubility of the gas washed by potash-lye is greater than when washed by conc. sulphuric acid. According to C. F. Schönbein, **hydrogen dioxide** in excess converts nitric oxide into nitric acid, and if not in excess, some nitrous acid is formed ; if the soln. be shaken with ether, and the nitrous acid be removed by alkali-lye, the neutral ethereal layer, when treated with an acid, yields nitrous acid. L. Spiegel suggested that the acid is formed by the action of the ozonized ether on atm. nitrogen. H. Wilfarht determined nitric oxide by transforming it into nitrate by an alkaline soln. of hydrogen dioxide, and titrating back with a standard soln. of potassium permanganate.

H. Moissan and P. Lebeau [7] found that nitric oxide reacts immediately with **fluorine** with the production of a pale yellow flame, and when the nitric oxide is in excess no volatile compound of fluorine is obtained, but the heat developed by the reaction decomposes the nitric oxide into nitrogen and oxygen, the oxygen reacting with the excess of nitric oxide to form nitrogen peroxide. By the action of nitric oxide on excess of fluorine at the temp. of liquid oxygen, a white solid is obtained, nitroxyl fluoride, $4NO+F_2=N_2+2NO_2F$. According to J. L. Gay Lussac, a mixture of nitric oxide with half its vol. of **chlorine** at —15° to —20° forms a pale orange-yellow gas which condenses to a dark brown liquid which is a mixture of nitrosyl and nitroxyl chlorides. E. Davy, and C. F. Schönbein studied this reaction, and **bromine** and **iodine** were found to react similarly. M. Berthelot said that nitric oxide is soluble in bromine. H. H. Landolt found that bromine reacts with nitric oxide, forming bromonitrous acid, or bromonitric acid, NO_2Br_2 or $NOBr_3$; but O. Fröhlich said that only nitrosyl bromide, NOBr, is formed, and that H. H. Landolt's products were a mixture of nitrosyl bromide and bromine. C. F. Schönbein found that nitric oxide reacts on iodine suspended in water, forming hydriodic and nitric acids. M. Trautz and F. A. Henglein observed no signs of ionization during the reaction: $2NO+Cl_2\rightleftharpoons 2NOCl$, and the reaction $2NO+Br_2\rightleftharpoons 2NOBr$. A. Pinkus said that ionization occurs in the former case if the chlorine be in excess, but this could not be confirmed. W. H. Rodebush and T. O. Yntema observed that a mixture of **hydrogen chloride** and nitric oxide, when cooled to the temp. of liquid air, furnishes a purple solid; this melts to a purple liquid between —153° and —143°, when it has a sp. conductivity of 10^{-3} ohms, a value near that for $0{\cdot}01N$-KOH. The vap. press. of the purple liquid is near that for liquid nitric oxide. It is assumed that an unstable complex is formed between —153° and 143°, and is possibly $(NOH)^+Cl^-$, *hyponitrous chloride*. E. T. Champman found that boiling conc. **hydriodic acid** absorbs nitric oxide slowly, forming ammonia and iodine. A. J. Balard showed that the reaction with **chlorine monoxide** is explosive: $Cl_2O+NO=NO_2+Cl_2$; and with **hypochlorous acid** and **hypochlorites,** chlorine and nitric acid are formed. H. Davy observed that red fumes are formed when nitric oxide is brought in contact with **euchlorine.** H. Reinsch found that when nitric oxide is passed into a flask of **hydrogen chloride,** a yellowish-green oily liquid is produced along with some colourless crystals which decompose with effervescence when treated with water. Both solid and liquid slowly decompose and give off chlorine. E. Briner and A. Wroczynsky found that in sealed tubes at 50 atm., a mixture of nitric oxide and hydrogen chloride does not change, but at 500 atm. press., the mixture condenses in liquid air to deep reddish-violet solid, doubtless an additive compound. At the ordinary temp., the highly compressed mixture is a colourless gas, which after a time deposits two liquids, the layers gradually increasing from day to day. The pale red layer is nitrosyl chloride, and the pale yellow layer is water containing dissolved nitrosyl chloride. The action $4NO+4HCl\rightarrow 2NOCl+2H_2O+Cl_2+N_2$ is strongly exothermic. If the tube contains excess of nitric oxide, the two liquid layers are slowly converted into one deep green liquid of unknown composition. R. Weber said that nitric oxide has no action on **potassium iodide.** According to H. A. Auden and G. J. Fowler, **potassium chlorate** is attacked at ordinary temp. by nitric oxide, forming chlorine, nitrogen peroxide, potassium nitrate, and a trace of perchlorate; K. A. Hofmann and co-workers found that the reaction begins at 210° with the production of potassium nitrate, chlorine, and oxygen; the reaction is faster at 300°. The liberated oxygen oxidizes the nitric oxide to some extent and some nitrite is formed. H. A. Auden and G. J. Fowler found that **barium chlorate** behaves similarly; and **silver chlorate** gives silver chloride, etc.; **potassium iodate** at 80° gives iodine and potassium nitrate; **silver iodate** at 110° forms silver iodide; **potassium perchlorate** is attacked at 300°, forming potassium nitrate; and **barium periodate,** $BaIO_4$, at 388° liberates iodine.

The flame of burning sulphur is extinguished in nitric oxide. According to G. Chevrier,[8] the passage of electric sparks through a mixture of nitric oxide and sulphur vapour results in the formation of nitrous acid, sulphur dioxide, and the so-called chamber crystals. C. Leconte found that equal vols. of **hydrogen sulphide** and nitric oxide react in a few hours, forming some nitrous oxide and ammonium sulphide. T. Thomson said the dried gases act most rapidly, but C. Leconte, and G. Lunge said that the dried gases do not react at all. S. Cooke noted that a mixture of hydrogen sulphide and nitric oxide can be exploded by electric sparks. G. Ville found that when nitric oxide is mixed with an excess of hydrogen sulphide, and passed over heated soda-lime, ammonia is formed. J. Priestley, and H. Davy observed the reduction of nitric to nitrous oxide by the action of **potassium sulphide,** dry, or in aq. soln. H. Davy found that pyrophoric potassium sulphide inflames in nitric oxide. Heated **barium sulphide** removes the oxygen from nitric oxide. A. Klemenc studied the oxidation of sulphides by nitric oxide. According to J. Pelouze, nitric oxide mixed with half its vol. of **sulphur dioxide,** standing over water, forms nitrous oxide and sulphuric acid ; R. Weber said that the transformation is not complete in 14 days at 22·5° ; but G. Lunge said the reaction is complete in 48 hrs., and all the nitric oxide is reduced to nitrous oxide ; a mixture of nitric oxide, sulphur dioxide and oxygen in the presence of water always forms some nitrous oxide, even when the oxygen is in excess. F. Kuhlmann showed that nitric oxide is reduced by sulphur dioxide in the presence of platinum sponge, forming nitrous oxide and water. The reaction proceeds quickly—particularly if the mixed gases be warmed. A. Klemenc, and L. Moser and R. Herzner studied the oxidization of sulphites by nitric oxide—*vide* the manufacture of sulphuric acid by the chamber process. L. Moser and R. Herzner found that the best mixture for absorbing nitric oxide contains 11–15 per cent. by wt. of anhydrous sodium sulphate, one per cent. of sodium hydroxide, and 88–84 per cent. of water. E. Briner and A. Wroczynsky found that a mixture of nitric oxide and sulphur dioxide in a sealed tube at 50 atm. press. does not change, but at 500 atm. press., a pale green solid is formed which is thought to be a soln. of nitric oxide in sulphur trioxide formed by the reaction : $2NO+2SO_2=2SO_3+N_2$. A. Graire observed that nitrous oxide is formed by the slow interaction of sulphur dioxide and nitric oxide in the liquid phase—*e.g.* as in a soln. of $FeSO_4.NO$. The reduction is increased by diluting the soln. ; it is feeble with 35 per cent. H_2SO_4, and takes place readily with 25 per cent. H_2SO_4. Only traces of nitrogen are produced. J. Priestley observed that **alkali sulphites** at ordinary temp. form nitrous oxide and ammonia ; and J. Pelouze found that **ammonium sulphite** acts similarly above 0°, but below that temp., it forms a complex salt, **ammonium nitrosylsulphite,** $NO(NH_4SO_3)$. E. Divers and T. Haga also produced **sodium dinitrosylsulphite,** $Na_2SO_3.2NO$, by the action of nitric oxide on an alkaline soln. of **sodium sulphite ;** similarly, with potassium sulphite, they obtained **potassium dinitrosylsulphite,** $K_2SO_3.2NO$. W. Manchot found that at 60° **sulphur trioxide** reacts with nitric oxide forming **nitrosylsulphur trioxide,** $2SO_3.NO$; the same product is produced by the action of sulphur dioxide on nitrogen peroxide (*q.v.*). The product melts at 215°–220° ; it softens at 180°, and boils at 275° and 715 mm. When heated it decomposes into sulphur dioxide and nitrogen peroxide. It is readily decomposed by water into sulphuric acid and nitric oxide ; but it does not react with a soln. of ferrous or cupric sulphate in conc. sulphuric acid. A. Graire observed that **sulphuric acid** is reduced by nitric oxide —*vide supra* for the solubility of the gas in the acid.

J. L. Gay Lussac [9] observed that a mixture of nitric oxide and **ammonia** decomposes slowly at ordinary temp., forming nitrogen and nitrous oxide ; and the mixture explodes when sparked. G. P. Baxter and C. H. Hickey said that the reaction : $6NO+4NH_3=5N_2+6H_2O$, is completed only at an elevated temp.—say by passing the mixture over copper turnings heated in a hard glass tube. W. Ramsay and J. T. Cundall were not able to demonstrate that nitric oxide and **nitrogen peroxide** unite at ordinary temp. ; but H. B. Dixon and J. D. Peterkin inferred that on mixing these two gases there is a limited combination. G. Lunge and G. I. Porschneff observed no change in vol. and no combination on mixing these gases above 28° ; at −21° and below, nitric oxide is freely absorbed by liquid nitrogen peroxide, forming blue liquid nitrogen trioxide (*q.v.*). A similar result is obtained by cooling a mixture of the two gases. These results contradict the conclusions drawn by W. Ramsay, and C. W. Hasenbach. H. le Blanc and W. Nuranen said that there is a state of equilibrium between the two gases $NO+NO_2\rightleftharpoons N_2O_3$ which, at ordinary temp., is almost wholly in favour of the mixture indicated on the left side of the equation—*vide infra,* nitrogen trioxide. According to V. H. Veley, nitrous acid is formed when nitric oxide is passed into conc. **nitric acid,** for, as dry nitric oxide is passed into monohydrated nitric acid, the liquid becomes yellow, then orange-red, and soon a red oil separates out; later, the liquid becomes blue, forming nitrogen peroxide, and finally nitrous acid. L. Marchlewsky said that with an acid of sp. gr. 1·510, the colour is brown; sp. gr. 1·410, yellow; 1·320, greenish-blue; and acids with a smaller sp. gr. are not coloured by nitric oxide. P. T. Austen also discussed this reaction—*vide infra,* nitrous acid. A. V. Schaposchnikoff's observations on the equilibrium conditions in the reaction $2NO+HNO_3+H_2O \rightleftharpoons 3HNO_2$ are indicated below in connection with nitrous acid. A. Sanfourche said that nitric oxide reduces nitric acid, producing, with acid of 10 per cent. or lower concentration, nitrous acid only ($2NO+HNO_3+H_2O \rightarrow 3HNO_2$); when the concentration of the nitric acid is in the neighbourhood of 20 per cent. a second reaction ($NO+2HNO_3 \rightarrow H_2O+3NO_2$) also occurs. The latter predominates with increasing concentration of the acid; with 70 per cent. acid, the former ceases.

According to H. Davy,[10] and J. L. Gay Lussac, feebly burning **phosphorus** is extinguished by nitric oxide, but if vigorously burning, the combustion continues as brilliantly as in oxygen, forming nitrogen, and phosphorus pentoxide. According to J. Dalton, nitric oxide is reduced in a few hours by spontaneously inflammable **phosphine,** forming nitrogen and nitrous oxide. The mixture is ignited by electric sparks, or by the addition of a little oxygen, forming water, nitrogen, and phosphoric acid. H. Reinsch reported a compound of nitric oxide and **phosphoric acid**—namely, *nitrosyl phosphoric acid;* H. Davy, and J. L. Gay Lussac found that red-hot **arsenic** absorbs oxygen and leaves half a vol. of nitrogen. H. Reinsch reported a compound of nitric oxide and **arsenic acid**—namely, *nitrosylarsenic acid.* A. Gutmann found that nitric oxide reacts with **sodium arsenite:** $2NO+Na_3AsO_3=N_2O+Na_3AsO_4$; and the same change occurs when sodium arsenite is added to a soln. of nitric oxide in freshly prepared, strongly alkaline soln. of potassium sulphite. The reaction was also studied by A. Klemenc.

H. St. C. Deville and F. Wöhler showed that when heated with amorphous **boron,** nitric oxide forms nitrogen, boron oxide, and nitride. F. Kuhlmann reported compounds of nitric oxide with **boron fluoride**—namely, *boron nitrosylfluoride;* and **silicon fluoride**—namely, *silicon nitrosylfluoride.* The combustion of **charcoal** in nitric oxide is more brilliant than in air, and J. Dalton found that the reaction is that symbolized by $2NO+C=CO_2+N_2$. H. Moissan said that **calcium carbide** at a dull red-heat readily oxidizes in an atm. of nitric oxide, and the reaction is vigorous at a higher temp., forming fused lime, and nitrogen. F. Kuhlmann observed that some cyanide is formed when the vapour of ethyl nitrate is passed over platinum sponge at 400°; but C. Weltzien observed no trace of hydrogen cyanide after the passage of a mixture of nitrogen trioxide and ethane over red-hot chromic oxide. L. I. de Nagy Ilosva found some hydrogen cyanide is formed when nitric oxide mixed with air is burnt in an atmosphere of **coal-gas;** and A. K. Huntington, that hydrogen cyanide is found amongst the products of the explosion of a compressed mixture of nitric oxide and **acetylene.** E. Elöd and H. Nedelmann studied the synthesis of hydrogen cyanide in the reaction between nitric oxide and hydrocarbons—**methane,** acetylene, and **ethylene**—in the presence of a mixture of quartz and alumina as catalyst. W. Henry referred to the vivid combustion which occurs when an electric discharge from a Leyden jar is passed through a mixture of ethylene and nitric oxide (nitrous gas), but with a small spark without a condenser in circuit the mixture is not inflamed; he also said that a mixture of **carbon monoxide** and nitric oxide cannot be inflamed by electric sparks, although, as S. Cooke showed, there is a gradual reduction of the nitric oxide: $2NO+2CO=2CO_2+N_2$. E. Briner and A. Wroczynsky observed no reaction between nitric oxide and carbon monoxide at 50 atm. press., but at 500 atm. press., there is evidence of chemical change; likewise also with mixtures of nitric oxide and **methyl chloride.** G. Baume and A. F. O. Germann obtained evidence of the formation of **methyl ether** and nitric oxide, **methyl dinitrosyl oxide,** $(CH_3)_2{=}O{=}(NO)_2$, of m.p. −166·3°, on the fusion curve. J. J. Berzelius said that a mixture of nitric oxide with the vapour of **carbon disulphide,** gives *ein grosse, schön leuchtende grünliche Flamme,* which in brilliancy resembles that of burning zinc. The flame is very rich in actinic rays, and special arrangements have been made for burning the mixture. The subject has been studied by E. Sell and R. Bidermann, C. Zenghelis, A. B. Delachanal and A. E. Mermet, and M. Tiffereau. For the solubility of nitric oxide in carbon disulphide, *vide supra.* H. Delbrück found that **potassium carbonyl** reacts with nitric oxide at a red-heat, forming potassium cyanide. According to M. Berthelot, nitric oxide forms a blue compound with **nickel tetracarbonyl.** R. L. Mond and A. E. Wallis could not isolate the product in a high state of purity, but they believe it to be **nickel dinitrosyl,** $Ni(NO)_2$, which dissociates violently at 90°. The reaction with **cobalt tetracarbonyl** furnishes **cobalt nitrosyltricarbonyl,** $Co(CO)_3.NO$; there is only a very slight reaction between nitric oxide and **cobalt tricarbonyl**; and **ferric enneacarbonyl** furnishes **iron nitrosylpentadecacarbonyl,** $Fe_4(NO)(CO)_{15}$—*vide* **5.** 39, 27. O. Baudisch found that organic nitrogenous products are produced by the action of light on mixtures of **formaldehyde** and nitric oxide. A. Miolatti described a number of complex **cyanogen compounds.** Numerous compounds of nitrosyl with **organic radicles** have been reported.[11] W. Traube, G. W. MacDonald and O. Masson, and M. Stechoff investigated the action of nitric oxide on an alcoholic soln. of sodium ethoxide resulting in the formation of $CH_2\{N(NO).ONa\}_2$; W. Traube regarded the compound $CH_2(N_2O_2Na)_2$ as representative of a series of compounds which he called *isonitramines.* He added that sodium ethoxide soln. do not react with nitric oxide so long as they are undecomposed, but as soon as ketones are formed by the autodecomposition of the sodium ethoxide soln., reaction sets in. F. Garelli noted the tendency of nitric oxide to enter the solid phase when soln. in benzene, bromoform, nitrobenzene, and cyclohexane are frozen, and so lower the f.p. from 0·25° to 0·225°. R. Seeliger studied the absorption of nitric oxide by dehydrated chabazite.

According to J. L. Gay Lussac,[12] L. J. Thénard, F. Kuhlmann, J. W. Döbereiner, and R. Hare, **potassium** burns when heated in nitric oxide, forming nitrogen and potassium oxide, which later produces some nitrite. A. Joannis observed that a hyponitrite is formed by the action of nitric oxide on **sodammonium** or **potassammonium.** H. Moissan showed that calcium takes fire in nitric oxide below a red-heat, burning with *une lumière éblouissante,* and forming fused calcium oxide but no nitride. P. Sabatier and J. B. Senderens found that **copper** acquires a superficial film of oxide when exposed to the gas; and reduced copper at 200° forms red cuprous oxide. A mixture of nitric oxide and hydrogen acts on reduced copper at 180°. forming ammonia, water, and nitrogen. T. Gray, and F. Emich studied the action of nitric oxide on heated copper. E. Müller and H. Barck said that copper decomposes 99·7 per cent. of the gas at 500°, but at lower temp. the action depends on the purity of the metal. E. Schröder and G. Tammann studied the rate of oxidation of copper by nitric oxide. No effect was observed when **silver** is exposed to nitric oxide; this is also the case with other metals which are not oxidized in air—*e.g.* **platinum.** E. Müller and H. Barck observed that silver is without action up to 700°; while **calcium** and **magnesium** decompose the gas at 500°, forming the oxides and nitrides; **brass** is without action at 600°, and decomposes only 29 per cent. at 700°; **zinc** has no action below 350°; at 600°, the action is slow, but decomposition is complete. P. Sabatier and J. B. Senderens found that, in general, moist metal reducing agents change nitric into nitrous oxide. Zinc and **cadmium** become superficially coated with oxide when exposed to the gas. J. Priestley observed that zinc reduces moist nitric oxide to nitrous oxide and ammonia; N. H. Morse and J. White, and F. Emich studied the action of nitric oxide on heated zinc. The latter also examined the action with cadmium. P. Sabatier and J. B. Senderens found that **mercury** is not perceptibly oxidized by nitric oxide at 450°, and F. Emich observed no action at the b.p. P. Sabatier and J. B. Senderens found that **aluminium** filings are very little changed by nitric oxide ; F. Emich examined the action of nitric oxide on **tin** and **lead**—in the former case stannic oxide is formed, and in the latter, lead oxide. P. Sabatier and J. B. Senderens noted that lead quickly acquires a film of lead oxide. E. Müller and H. Barck said that tin has no action up to 400°, but then commences to act rapidly, forming a nitride which may be completely decomposed at 600°. They also found that **aluminium** has little action below 600° ; **chromium** has no action below 700° ; **ferrochrome**—with 60 per cent. chromium—decomposes 19 per cent. of the gas at 650° ; and **manganese** decomposes 68 per cent. of the gas at 400° and all of it at 500°, forming manganese nitride. F. Emich also observed the effect of nitric oxide on heated **titanium,** chromium, **molybdenum, tungsten, uranium,** and manganese. E. Müller and H. Barck found that **bismuth** decomposes 74 per cent. of the gas at 400°, forming bismuth trioxide. Vanadium trioxide is formed when **vanadium** is heated in an atm. of nitric oxide. P. Sabatier and J. B. Senderens observed that at ordinary temp., **iron** acquires a superficial film of oxide. I. Milner found that moist iron filings and nitric oxide form ammonia ; J. Priestley noted that nitrous oxide as well as ammonia is formed ; and P. Sabatier and J. B. Senderens obtained nitrogen, nitrous oxide, and a little hydrogen and ammonia. With moist iron filings and sulphur, C. L. Berthollet obtained 44 vols. of nitrogen from 100 vols. of nitric oxide. H. Buff and A. W. Hofmann found an electrically heated iron spiral burns in nitric oxide. According to P. Sabatier and J. B. Senderens, reduced iron at 200° glows and forms black ferrous oxide. E. Müller and H. Barck said that iron reduced in hydrogen decomposes nitric oxide better than copper. E. Schröder and G. Tammann studied the rate of oxidation of iron and **nickel** by nitric oxide. The action of nitric oxide on heated iron, **cobalt,** and nickel was studied by F. Emich, Reduced cobalt at 150° forms brown cobalt oxide ; and reduced nickel at 200° forms brown nickel oxide ; and reduced nickel at 200° forms yellowish-green nickel oxide. A mixture of nitric oxide and hydrogen in the presence of warm reduced nickel furnishes ammonia. From his observations on the action of nitric oxide on the metals, F. Emich concluded that the action closely resembles, but is much slower than, that of oxygen provided the temp. of the former gas is kept below the point at which dissociation occurs. Of the metals examined, only copper, lead, and vanadium give products different from those obtained with oxygen ; and mercury is not attacked by nitric oxide below its b.p. E. Schröder and G. Tammann compared the rates of oxidation of metals—copper, iron, and nickel—in oxygen, nitric oxide, and nitrous oxide. In general, C. B. Bazzoni and A. T. Waldie said that hot metals—*e.g.* nickel—decompose nitric oxide, forming the metal oxide and nitrogen.

B. C. Dutt and S. N. Sen found that when nitric oxide is passed into a suspension of **barium dioxide** in water, barium nitrite, not nitrate, is formed. P. Sabatier and J. B. Senderens observed no change when nitric oxide is passed over **cuprous oxide** at 500°. H. A. Auden and G. J. Fowler observed that dry nitric oxide and **silver oxide,** at ordinary temp., form silver and silver nitrate ; P. Sabatier and J. B. Senderens also obtained silver and silver nitrite by passing nitric oxide into water with silver oxide in suspension. C. F. Schönbein found **gold oxide** is reduced by moist nitric oxide, forming nitrous acid. P. Sabatier and J. B. Senderens found that **titanium sesquioxide** forms white titanic oxide when heated in an atm. of nitric oxide ; and that **stannous oxide** below 500° burns in an atm. of nitric oxide, forming stannic oxide. If nitric oxide be passed into water with **lead dioxide** in suspension, the water is coloured, and in about 3 hrs., lead nitrite and nitrate are formed, and later, rhombic crystals of a basic nitrite. B. C. Dutt and S. N. Sen said that the nitrate is formed by the action of the dioxide on the nitrite. Lead dioxide is reduced to lead oxide by nitric oxide at 315°, and H. A. Auden and G. J. Fowler found that the reaction begins at 15°, when a basic lead nitrite is formed ; the maximum speed of the reaction occurs at 130°. E. Müller and H. Barck observed that at room temp. lead dioxide absorbs nitric oxide, forming the nitrite ; on heating, the gas is liberated, but at 200°, oxygen is liberated as well, and nitrogen peroxide is formed ; **red-lead** has no action on the gas at room temp., but complete absorption occurs at 200° ; while **lead monoxide** is practically without action on nitric oxide even at 650°. P. Sabatier and J. B. Senderens observed that in an atm. of nitric oxide at a bright red-heat, **molybdenum sesquioxide** forms the dioxide ; **tungsten dioxide,** at about 500°, forms the blue higher oxide ; and **uranium dioxide** forms the pentoxide ; while **vanadium trioxide** is not attacked below 500°, but E. Müller and H. Barck observed that the gas at 500° is completely decomposed and vanadium tetroxide is formed. Manganous oxide, at a red-heat, forms brown Mn_3O_4 ; so also does **manganese dioxide** at 400°—H. A. Auden and G. J. Fowler said that the reaction is very slow at ordinary temp., and fast at 216°. C. F. Schönbein observed that manganese dioxide suspended in water slowly forms nitrite when in the presence of nitric oxide. I. M. Kolthoff observed that permanganates in acid soln. completely oxidize nitrous acid in 15 minutes. J. Gay observed that freshly precipitated ferrous oxide reduces nitric oxide to nitrogen.

The absorption of nitric oxide by soln. of **copper salts** has been previously discussed. E. Drechsel found that Fehling's solution is reduced to cuprous oxide by nitric oxide. A. Besson obtained **aluminium nitrosylhexachloride,** $2AlCl_3.NO$, by the action of nitric oxide on dry **aluminium chloride.** E. Ludwig and T. Heim found that nitric oxide is reduced by a hot, conc., acidified soln. of **stannous chloride,** forming hydroxylamine, but the metal and cold dil. acid give a better yield. E. J. Maumené also obtained hydroxylamine by the reducing action of stannous chloride. E. Divers and T. Haga said that part of the nitric oxide is reduced to nitrogen, and added :

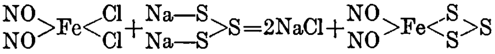
> There is a remarkable fact about the reaction between nitric oxide and stannous chloride. At a temp. of fully 100°, there is no action between nitric oxide and acid stannous chloride soln. The stannous chloride remains unchanged for hours together, and neither nitrogen nor hydroxylamine is formed. The only thing we have noticed is always a trace of ammonia in experiments at 100°, and this, we are inclined to believe, is due to some other cause than this reaction alone. At 90°, the action is still exceedingly small, but as the temp. descends from about 80°, it becomes rapidly greater with the descent.

O. von Dumreicher did not agree with this ; he found that at 100°, both nitric oxide, and hydroxylamine are reduced to ammonia by an acidified soln. of stannous chloride. At room temp., the yield is poor with acidified stannous chloride although it is quantitative with tin and hydrochloric acid. F. Kuhlmann prepared a complex salt with **stannic chloride**—namely, *stannic nitrosylchloride,* $SnCl_4(NO)$—which is thought by R. Weber, and W. Hampe to be $SnCl_4.2NOCl$ —*vide infra.* O. von Dumreicher reduced nitric oxide by **stannous chloride,** forming hydroxylamine (*q.v.*), and ammonia (*q.v.*) ; and E. Divers and T. Haga obtained only hydroxylamine and nitrogen, no nitrous oxide or ammonia. With **potassium stannite** in alkaline soln., nitric oxide forms the hyponitrite (*q.v.*). H. Reihlen and A. Hake prepared a number of complex salts of **titanium tetrachloride** with organic nitro- and nitroso-compounds. Titanium tetranitrate, $Ti(NO_2)_4$, or chlorotrinitrate forms **titanium dinitrosylhexachloride,** $TiCl_6(N_2O_2)$, as a yellow, fuming salt. V. Thomas observed that if dry **bismuth chloride** be in contact with nitric oxide for a day, **bismuth nitrosyltrichloride,** $BiCl_3(NO)$, is formed. A. Besson obtained this product and also yellow crystals of **antimony nitrosyldecachloride,** $2SbCl_5.NO$, by the action of nitric oxide on anhydrous **antimony pentachlorde.** For the action of nitric oxide on **chromous chlcride,** *vide supra.* G. Chesneau observed that a blue soln. of chromous chloride reduces nitric oxide to hydroxylamine when the gas is run in rapidly, and to ammonia when run in slowly. V. Kohlschütter found that the nitric oxide is reduced to hydroxylamine in acidic soln., and to ammonia in neutral soln. This is in agreement with the general observations by M. L. Nichols and I. A. Derbigny that increased acidity lowers the reduction potential of most reducing agents faster than it increases the oxidizing power of nitrogenous gases. P. Sabatier and J. B. Senderens, and C. Böhmer found that chromic acid reacts with nitric oxide at ordinary temp. H. A. Auden and G. J. Fowler found dry **lead chromate** remains unchanged at 400°; and **silver chromate** at 300° forms silver, silver nitrate, and chromic oxide. A. Werner and G. Richter obtained **chromic nitrosyl tetrathiocyanatodiammine,** $[Cr(NH_3)_2(SCy)_4]NO$, by the action of 10 per cent. nitric acid on potassium or ammonium tetrathiocyanatodiammine. The dark brown, four-sided prisms are unstable, and they are decomposed by water, and alkali-lye. The vapour of **chromyl chloride** was found by V. Thomas to react with nitric oxide, forming a complex $Cr_5Cl_5O_7.2NO$, *chromium nitrosyloxychloride.* For the action of nitric oxide on **manganous chloride,** *vide supra.* C. F. Schönbein found that **permanganic acid** oxidized nitric oxide to nitric acid; alkaline soln. of **potassium permanganate** greedily absorb nitric oxide at ordinary temp., and manganese dioxide separates out. This reaction was studied by C. Böhmer, B. C. Dutt and co-workers, and A. Cavazzi. G. Lunge determined nitric oxide volumetrically by titration with permanganate: $10NO+6KMnO_4+9H_2SO_4=10HNO_3+6MnSO_4+3K_2SO_4+4H_2O$. Dry potassium permanganate was found by H. A. Auden and G. J. Fowler to react with nitric oxide at 190°, forming manganese dioxide and potassium nitrate; while **silver permanganate** at 80° forms silver, silver oxide and nitrate, and manganese dioxide.

The action of nitric oxide on **iron, cobalt, and nickel salts** has been previously discussed. Complexes with iron salts and nitrosyl have been discussed by W. Manchot[13] and co-workers, A. Werner, K. A. Hofmann and O. F. Wrede, C. Marie and R. Marquis, and I. Bellucci and D. Venditori. W. Manchot and A. Waldmüller obtained with **palladium salts** the complexes **palladous dinitrosylchloride,** $PdCl_2.2NO$, and **palladous dinitrosylsulphate,** $PdSO_4.2NO$. They are unstable salts giving off nitric oxide in the presence of water. Nitric oxide with palladous nitrate yields $Pd(NO_2)_2$. Hence, nitric oxide is known to form complexes with the salts of Cu, Mn, Fe, Co, Ni, and Pd.

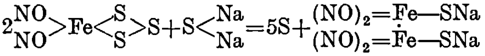
In 1858, Z. Roussin[14] discovered that a definite compound, which he called *binitrosulfure de fer*, can be formed by the simultaneous action of an alkali nitrite and sulphide on an iron salt, just as a nitroferricyanide is formed by the joint action of an alkali nitrite and cyanide on an iron salt. Z. Roussin made this compound by adding a soln. of ferrous or ferric chloride slowly to a mixed soln. of potassium nitrite and ammonium sulphide, and then boiling the mixture for a few minutes. If ferric chloride is used some sulphur is formed. The filtered liquid furnishes black, rhombic needles of the so-called *Roussin's black salt.* This compound was also obtained by A. Porzczinsky by warming ammonium sulphide with a soln. of ferrous salt sat. with nitric oxide—*vide infra.* The black crystals were said by A. Porzczinsky to be monoclinic; and by J. O. Rosenberg, triclinic. The crystals were found by Z. Roussin to be stable in air when separated from alkaline soln., but if pure, A. Porzczinsky, and J. O. Rosenberg said that they easily give off nitric oxide when exposed to air. The crystals are stable at 100°; but at 110°, they were found by J. O. Rosenberg to begin to give off water of crystallization. Z. Roussin found that the salt begins to decompose when heated above 115° giving off red fumes, and forming sulphur, and ammonium sulphite and nitrite. At ordinary temp., 100 parts of water dissolve 0·893 part of salt, and at 100°, 50 parts of salt. The soln. is dark brown, one part of salt in 20,000 parts of water is distinctly coloured; the soln. has a styptic and bitter taste. The salt is precipitated from its aq. soln. by the addition of a soln. of potassium hydroxide, ammonia, or ammonium sulphide. At ordinary temp., chlorine, and iodine, as well as the mineral acids, decompose the salt, and this more quickly at a higher temp. The salt is not affected by organic acids; it is freely soluble in alcohol, and in ether; it is insoluble in chloroform, and in carbon disulphide. Many metallic salts decompose a soln. of the salt liberating nitric oxide; while potassium cyanide forms the nitroferricyanide. Z. Roussin's analysis of his *binitrosulfure de fer* corresponded with $Fe_3S_5H_2N_4O_4$; A. Porzczinsky's, with $Fe_3S_3N_4O_4.2H_2O$; and J. O. Rosenberg's, with $Fe_6S_5N_{10}O_{10}.4H_2O$. The products here analyzed were probably impure, because I. Bellucci and P. de Cesaris's, O. Pavel's, L. Marchlewsky and J. Sach's, and W. Manchot and E. Linckh's analyses correspond with $KFe_4(NO)_7S_3$. I. Bellucci and F. Carnevali found that the effect of the black sodium and potassium salts on the f.p. of water, and acetone, and of the potassium salt on the f.p. of nitrobenzene corresponds with a mol. wt. one-half the formula of **potassium ferroheptanitrosylsulphide,** $K[Fe_4(NO)_7S_3]H_2O$. This indicates that in dil. soln., the salt is completely ionized. The mol. conductivity of the black sodium salt also agrees with the assumption that the sodium salt is the salt of a monobasic acid. According to O. Pavel, and I. Bellucci and co-workers, when the sodium or potassium salt is treated with dil. sulphuric acid, it furnishes a brown, amorphous mass supposed to be **hydrogen ferroheptanitrosylsulphide,** $H[Fe_4(NO)_7S_3]$. O. Pavel showed that this compound is unstable; it is insoluble in water, alcohol, and ether; but soluble in chloroform, and in carbon disulphide.

Z. Roussin found that if the black sodium salt be treated in the cold with a little acid, a yellowish-red flocculent precipitate of what he called *nitrosulfure sulfuré de fer*, $Fe_2S_3N_2O_2.4H_2S$, is formed; but if the soln. be boiling, when treated with an excess of acid, what he called *nitrosulfure de fer*, $Fe_2S_3N_2O_2$, is formed as an unstable, black precipitate. According to I. Bellucci and co-workers, when a $0{\cdot}1N$-soln. of sodium trisulphide is mixed with a soln. of ferrous chloride sat. with nitric oxide at about —2°, dark brown **ferrous dinitrosyltrisulphide,** $Fe(ON)_2S_3$, is formed:



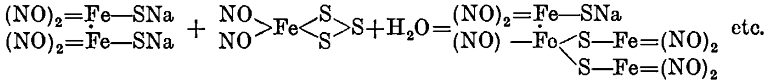
$$\begin{matrix}\mathrm{NO}\\\mathrm{NO}\end{matrix}\!>\!\mathrm{Fe}\!<\!\begin{matrix}\mathrm{Cl}\\\mathrm{Cl}\end{matrix}+\begin{matrix}\mathrm{Na-S}\\\mathrm{Na-S}\end{matrix}\!>\!\mathrm{S}=2\mathrm{NaCl}+\begin{matrix}\mathrm{NO}\\\mathrm{NO}\end{matrix}\!>\!\mathrm{Fe}\!<\!\begin{matrix}\mathrm{S}\\\mathrm{S}\end{matrix}\!>\!\mathrm{S}$$

Sodium trisulphide gives a better yield than the mono- or the di-sulphide. Ferrous dinitrosyltrisulphide can be preserved under water. Z. Roussin observed that the evaporation of a soln. of *nitrosulfure de fer* in sodium sulphide furnishes red, prismatic crystals of *nitrosulfure de fer et de sodium*, $Fe_2S_4N_2O_2Na_2.H_2O$, a salt sometimes called *Roussin's red salt.* I. Bellucci and P. de Cesaris showed that the composition is $Fe_2S_4(ON)_4Na_2.4H_2O$, or $K[Fe(NO)_2S].2H_2O$—**potassium dinitrosylsulphide**—and they obtained it by treating ferrous dinitrosyltrisulphide with $0{\cdot}04N$-sodium sulphide. The first product of the reaction:



$$2\begin{matrix}\mathrm{NO}\\\mathrm{NO}\end{matrix}\!>\!\mathrm{Fe}\!<\!\begin{matrix}\mathrm{S}\\\mathrm{S}\end{matrix}\!>\!\mathrm{S}+\mathrm{S}\!<\!\begin{matrix}\mathrm{Na}\\\mathrm{Na}\end{matrix}=5\mathrm{S}+\begin{matrix}(\mathrm{NO})_2{=}\dot{\mathrm{F}}\mathrm{e}{-}\mathrm{SNa}\\(\mathrm{NO})_2{=}\dot{\mathrm{F}}\mathrm{e}{-}\mathrm{SNa}\end{matrix}$$

is Roussin's red salt, which immediately changes into Roussin's black salt:



$$\begin{matrix}(\mathrm{NO})_2{=}\dot{\mathrm{F}}\mathrm{e}{-}\mathrm{SNa}\\(\mathrm{NO})_2{=}\dot{\mathrm{F}}\mathrm{e}{-}\mathrm{SNa}\end{matrix}+\begin{matrix}\mathrm{NO}\\\mathrm{NO}\end{matrix}\!>\!\mathrm{Fe}\!<\!\begin{matrix}\mathrm{S}\\\mathrm{S}\end{matrix}\!>\!\mathrm{S}+\mathrm{H_2O}=\begin{matrix}(\mathrm{NO})_2{=}\dot{\mathrm{F}}\mathrm{e}{-}\mathrm{SNa}\\(\mathrm{NO})\,{-}\dot{\mathrm{F}}\mathrm{e}\!<\!\begin{matrix}\mathrm{S}{-}\mathrm{Fe}{=}(\mathrm{NO})_2\\\mathrm{S}{-}\mathrm{Fe}{=}(\mathrm{NO})_2\end{matrix}\end{matrix}\quad\text{etc.}$$

Roussin's red salt. **Ferrous dinitrosyltrisulphide.** **Roussin's black salt.**

There are thus two series of nitrosylsulphides: (i) Ferrous dinitrosyl-derivatives (Roussin's red salts); and (ii) Ferrous heptanitrosyl-derivatives (Roussin's black salts). If sufficiently conc. soln. of ferrous dinitrosyltrisulphide in alkali sulphide be used, the red salt crystallizes out before the black salt begins to form. This occurs, for instance, if N-Na_2S be used in place of the $0{\cdot}04N$-soln. The red salt is also produced by decomposing ferrous dinitrosyltrisulphide with a hot soln. of potassium hydroxide. The red salt is converted into the black salt under the influence of carbon dioxide, dil. acids, or ferrous chloride: $4K_2Fe_2(NO)_4S_2+2CO_2+2H_2O=2KFe_4(NO)_7S_3+2H_2S+K_2N_2O_2+2K_2CO_3$; and the black salt is converted into the red salt by treatment with alkali hydroxide: $2KFe_4(NO)_7S_3+4KOH=3K_2Fe_2S_3(NO)_4+Fe_2O_3+N_2O+2H_2O$, or else $2KFe_4(NO)_7S_6+6KOH=3K_2S_2(NO$

$+4Fe_2O_3+3H_2O+K_2N_2O_2$. If cadmium oxide be present, both the red and the black salts give off all their nitrogen as nitrous oxide which is formed by the oxidation of ferrous iron $2FeO+2NO=Fe_2O_3+N_2O$. When Roussin's black salt is heated with dil. sulphuric acid and silver sulphate, it gives off nitric oxide eq. to 4 gram-atoms of nitrogen per mol, and nitrous oxide eq. to 3 gram-atoms of nitrogen per mol. Under similar circumstances, Roussin's red salt yields the mixture $2NO+2N_2O$. The formation of nitrous oxide is due to the oxidation of ferrous iron as just indicated. If a mol. of potassium ferroheptanitrosylsulphide be treated with copper sulphate, seven mols. of nitric oxide are given off, and the cupric salt is reduced to the cuprous state. According to L. Cambi, if the ferroheptanitrosylsulphide be treated with silver nitrate, silver hyponitrite is formed: $2KFe_4(NO)_7S_3+26AgNO_3=2KNO_3+8Fe(NO_3)_3+6Ag_2S+7Ag_2N_2O_2$. I. Bellucci and P. de Cesaris found that when the compound is treated with potassium permanganate, the equivalent of 26 gram-atoms of oxygen are required to oxidize all the elements in a mol. of the ferroheptanitrosyltrisulphide. This is in agreement with the assumption that all the iron in the mol. is present in the ferrous condition. L. Cambi suggested that the ferroheptonitrosyltrisulphides are complexes of sulphides and hyponitrites, possibly of the form $K_2N_2O_2.2FeS_3.2Fe_2(N_2O_2)_3$; but a comparison of the behaviour of this salt with that of the complex sulphides $Fe_2S_3.K_2S$, and $2FeS.K_2S$, towards hydrochloric acid, was found by I. Bellucci and P. de Cesaris to be in agreement with the assumption that the three atoms of sulphur in the mol. are probably sulphidic, and combined directly with the iron atoms.

The ferroheptanitrosyl-derivatives or Roussin's black salts of the type: $R'[Fe_4(NO)_7S_3]$, are represented by the potassium salt indicated above. O. Pavel obtained the potassium salt by adding 400 c.c. of potassium sulphide—prepared from 44 grms. potassium hydroxide—to a boiling soln. of 35 grms. of sodium nitrite in 400 c.c. of water. After the addition of a few drops of dil. sulphuric acid, 159 grms. of ferrous sulphate dissolved in 1200 c.c. of water are slowly poured into the hot mixture. The liquid is heated in a water-bath for about half an hour, until a deposit begins to settle on the sides of the flask. It is then quickly filtered, and dil. potassium sulphide is added to the filtrate. After 48 hrs., the potassium salt crystallizes out. It is purified by recrystallization at 70° from water, containing a small quantity of potassium hydroxide. O. Pavel prepared **lithium ferroheptanitrosyltrisulphide** by the method emphasized for the potassium salt. O. Pavel, and I. Bellucci and co-workers prepared **sodium ferroheptanitrosyltrisulphide,** $Na[Fe_4(NO)_7S_3].2H_2O$, in an analogous manner. O. Pavel found that the sodium salt is completely decomposed by hot, conc. sulphuric acid, by silver oxide or sulphate, by hydrochloric acid, and by iodine. W. Manchot and E. Linckh studied the absorption spectra of soln. of the ferroheptanitrosyltrisulphides. They found that the absorption spectra bear no relation to that of the $FeSO_4.NO$-salts, and they assumed that the iron is univalent. On the other hand, L. Cambi and L. Szegö found the absorption spectra of dil. soln. indicate the presence of bivalent iron as in the case of $FeSO_4.NO$. O. Loew reported *sodium ferrohexanitrosylthiocarbonate*, $Fe_4(NO)_6CS_3$, to be formed by the action of ferrous sulphate on a mixture of sodium thiocarbonate and nitrite, but O. Pavel showed that the product is really sodium ferroheptanitrosyltrisulphide; and he prepared **ammonium ferroheptanitrosyltrisulphide,** $NH_4[Fe_4(NO)_7S_3].H_2O$, by the method employed for the potassium salt; it is less soluble than the potassium salt. Similarly with **rubidium ferroheptanitrosyltrisulphide**, which is less soluble than the ammonium salt; while **cæsium ferroheptanitrosyltrisulphide** is insoluble in cold water, and sparingly soluble in alcohol and ether. According to I. Bellucci and C. Cecchetti, a number of other salts can be prepared in stable, shining, black crystals, which can be crystallized from water, and remain unchanged for a long time if preserved in the absence of light. Thus, if the sodium salt be treated with hydrazine in acidic or alkaline soln., **hydrazine ferroheptanitrosyltrisulphide,**

$N_2H_4.H[Fe_4(NO)_7S_3]$, is formed; it is slightly soluble in water, and freely soluble in alcohol or ether. If hydroxylamine in acidic or alkaline soln. be employed in place of hydrazine, **hydroxylamine ferroheptanitrosyltrisulphide**, $NH_2OH.H[Fe_4(NO)_7S_3]$, is formed; it is readily soluble in water, alcohol, and ether.

I. Bellucci and F. Carnevali observed that if the sodium salt be treated with phenylhydrazine hydrochloride, **phenylhydrazine ferroheptanitrosyltrisulphide**, $C_6H_5.N_2H_3.H[Fe_4(NO)_7S_3]$, is obtained; it melts under hot water in which it is sparingly soluble; it is freely soluble in alcohol and ether, but sparingly soluble in benzene. Similarly, **carbazide ferroheptanitrosyltrisulphide**, $N_2H_3.CO.NH_2.H[Fe_4(NO)_7S_3]$, has been prepared; it is soluble in water, alcohol, and ether. They also prepared **tetramethylammonium ferroheptanitrosyltrisulphide**, $N(CH_3)_4[Fe_4(NO)_7S_3]$, which, in acetone soln., yields black, triclinic crystals with the axial ratios $a:b:c=0{\cdot}8648:1:1{\cdot}3125$, and $\alpha=87°\ 29'\ 34''$, $\beta=106°\ 7'\ 10''$, and $\gamma=93°\ 44'\ 10''$, and the sp. gr. 2·056 at 19°. It is sparingly soluble in water, and soluble in alcohol. Similarly, **tetraethylammonium ferroheptanitrosyltrisulphide**, $N(C_2H_5)_4[Fe_4(NO)_7S_3]$, furnishes black, triclinic crystals with the axial ratios $a:b:c=1{\cdot}0221:1:1{\cdot}0247$, and $\alpha=85°\ 8'\ 19''$, $\beta=97°\ 8'\ 2''$, and $\gamma=99°\ 17'\ 41''$, and sp. gr. 1·883 at 18°; it is sparingly soluble in water, alcohol, and benzene. These two salts are insoluble in ether, and are very stable, for they are not decomposed by boiling with a 50 per cent. soln. of potassium hydroxide. I. Bellucci and F. Carnevali also prepared **aniline ferroheptanitrosyltrisulphide**, $C_6H_5NH_2.H[Fe_4(NO)_7S_3]$, soluble in nitrobenzene, and aniline; moderately soluble in water, alcohol, ether, and benzene; and sparingly soluble in chloroform, and in benzene; **pyridine ferroheptanitrosyltrisulphide**, $C_5H_5N.H[Fe_4(NO)_7S_3]$, soluble in alcohol, ether, and acetone, and sparingly soluble in water; and *o*-**phenylenediamine ferroheptanitrosyltrisulphide**, $C_6H_4(NH_2)_2.H_2[Fe_4(NO)_7S_3]_2$, soluble in water, alcohol, acetone, and ether.

O. Pavel prepared **calcium ferroheptanitrosyltrisulphide** by the method employed for the potassium salt. It is freely soluble in water; similarly also with **barium ferroheptanitrosyltrisulphide**, and with **magnesium ferroheptanitrosyltrisulphide.** These salts are decomposed by heat in the presence of air, forming ammonium sulphate, ferrous sulphide, etc.; and if air be excluded, no ammonium sulphate is produced. O. Pavel, and L. Marchlewsky and J. Sachs prepared **thallium ferroheptanitrosyltrisulphide**, $Tl[Fe_4(NO)_7S_3].H_2O$, by the action of thallium sulphate on an aq. soln. of the alkali salt, and crystallized the product as rapidly as possible from alcohol in vacuo. It is sparingly soluble in water, and is decomposed by a protracted heating with water. I. Bellucci and F. Carnevali prepared **cobalt hexamminoferroheptanitrosyltrisulphide**, $Co(NH_3)_6[Fe_4(NO)_7S_3]_3$, soluble in water, alcohol, ether, and acetone.

The ferrodinitrosyl-derivatives or Roussin's red salts of the type $R'[Fe(NO)_2S]$ are represented by **potassium ferrodinitrosylsulphide**, $K[Fe(NO)_2S].2H_2O$, prepared, as indicated above, by the action of hot, dil. soln. of potassium hydroxide on the ferroheptanitrosyltrisulphides. O. Pavel prepared **sodium ferrodinitrosylsulphide**, $Na[Fe(NO)_2S].4H_2O$, in a similar way. These dark red coloured salts are unstable; they are, with the exception of the iron compound, insoluble in ether, chloroform, and carbon disulphide. They are decomposed by potassium ferricyanide, which does not attack ferroheptanitrosyltrisulphides. These salts decompose violently when heated, giving ammonium and alkali sulphates, etc. When the potassium salt is treated with dil. sulphuric acid, hydrogen ferrodinitrosylsulphide, $H[Fe(NO)_2S]$, is formed. This soon decomposes into hydrogen sulphide, nitrous oxide, nitrogen, and hydrogen ferroheptanitrosyltrisulphide. W. Manchot and E. Linckh studied the absorption spectra of soln. of ferrodinitrosylsulphides. O. Pavel prepared monoclinic crystals of **ethyl ferrodinitrosylsulphide**, $C_2H_5[Fe(NO)_2S]$, soluble in ether, benzene, chloroform, ethyl iodide, and carbon disulphide; while K. A. Hofmann and O. F. Wiede prepared tabular crystals of **phenyl ferrodinitrosylsulphide**, $C_6H_5[Fe(NO)_2S]$, melting at 179°, and giving, by the cryoscopic method, a mol. wt. corresponding with the doubled mol. If nitric oxide is passed into a soln. of ferrous sulphate and potassium thiosulphate for about 10 hrs., reddish-brown crystals of **potassium ferrodinitrosylthiosulphate**, $K[Fe(NO)_2(S_2O_3)].H_2O$, are formed. The crystals are soluble in water. Similarly with **sodium ferrodinitro-**

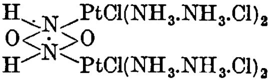
sylthiosulphate, and with **ammonium ferrodinitrosylthiosulphate**—the latter is more soluble than the former.

J. Sand and O. Genssler[15] obtained a series of complex salts by the action of nitric oxide on ammoniacal soln. of cobalt salts. They considered the products to be formed by the addition of two mols. of the cobalt pentammines. Thus, **cobalt nitrosylpentamminodichloride,** $[Co(NO)(NH_3)_5]Cl_2$, furnishes black crystals supposed to be constituted $Cl_2[(NH_3)_5Co.NO.NO.Co(NH_3)_5]Cl_2$ or $[Co_2(N_2O_2)(NH_3)_{10}]Cl_4$.

There is also a series of red salts supposed to have a different constitution. Thus, **cobalt nitrosylpentamminodinitrate,** $[Co(NO)(NH_3)_5](NO_3)_2.\frac{1}{2}H_2O$. This yields the complex salts *cobalt dinitrosyldecamminodinitratotetranitrate,* $[Co_2\{N_2O_2(NO_3)_2\}(NH_3)_{10}](NO_3)_4$; *cobalt dinitrosyldecamminosulphatotetranitrate,* $[Co_2\{N_2O(SO_4)\}(NH_3)_{10}](NO_3)_4$; *cobalt dinitrosylenneamminoiodotetraoxalate,* $[Co_2\{N_2O(C_2O_4)\}(NH_3)_9(H_2O)](H.C_2O_4)_4$; *cobalt dinitrosyldecamminodinitratotetraperchlorate,* $[Co_2\{N_2O(NO_3)_2\}(NH_3)_{10}](ClO_4)_4$; *potassium cobalt dinitrosyldecamminodiiododinitratoiodide,* $[Co_2(N_2O_2)(NH_3)_{10}](NO_3)_2I_2.KI$; *silver cobalt dinitrosyldecamminotetranitratonitrate,* $[Co_2(N_2O_2)(NH_3)_{10}](NO_3)_4.AgNO_3$; *lead cobalt dinitrosyldecamminotetranitratonitrate,* $[(Co_2(N_2O_2)(NH_3)_{10}](NO_3)_4.\frac{1}{2}Pb(NO_3)_2$.

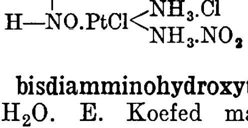
E. Koefed[16] prepared a number of complexes of nitric oxide and **platinum salts.** Thus, **platinous tetramminodichloronitrosylhydrochloride,** $Pt(NH_3)_4Cl_2.NO.HCl$, was considered by E. A. Hadow to have the formula $2Pt(NH_3)_4Cl_2.N_2O_3.2HCl$. It is obtained in green octahedral crystals by the action of nitrogen trioxide on a hydrochloric acid soln. of platinous tetramminodichloride; by the action of sodium nitrite on an ammoniacal soln. of potassium chloroplatinite; by passing nitric oxide into a hydrochloric acid soln. of potassium chloroplatinite; or by adding a soln. of ferrous sulphate sat. with nitric oxide into a hydrochloric acid soln. of platinous tetramminodichloride. The constitution is considered to be represented by one of the following schemes:

$$\begin{array}{l} H—\dot{N}O.PtCl(NH_3.NH_3.Cl)_2 \\ H—\dot{N}O.PtCl(NH_3.NH_3.Cl)_2 \end{array}$$



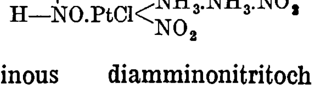
E. Koefed made **platinous tetramminodichlorodinitrosylhydrosulphate,** $[Pt(NH_3)_4Cl_2](NO)_2H_2SO_4$; **platinous tetramminodichloro-dichloronitrosylhydrochloride,** $[Pt(NH_3)_4Cl_2]Cl_2.NO.HCl$; and **platinous tetramminodinitratonitrosylhydronitrate,** $Pt(NH_3)_4(NO_3)_2.NO.HNO_3$.

S. Koefed prepared apple-green crystals of **platinous diamminonitritochloronitrosylhydrochloride,** $Pt(NH_3)_2(NO_2)Cl.NO.HCl.\frac{3}{4}H_2O$, by heating platinous tetramminodichloride with sodium nitrite and dil. hydrochloric acid on a water-bath, and drying the product at 100°. The constitution of the salt without water of hydration, is represented:



$$\begin{array}{l} H—NO.PtCl<\begin{smallmatrix}NH_3.Cl\\NH_3.NO_2\end{smallmatrix} \\ \quad\ \ | \\ H—NO.PtCl<\begin{smallmatrix}NH_3.Cl\\NH_3.NO_2\end{smallmatrix} \end{array}$$

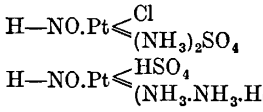
There is also a **platinous bisdiamminohydroxytriiodo-bisnitrosylhydroiodide,** $Pt_2(NH_3)_4(OH)I_3.2(NO.HI).6H_2O$. E. Koefed made bluish-green crystals of **platinous diamminodinitritonitrosylhydrochloride,** $Pt(NH_3)_2(NO_2)_2.NO.HCl$, by the action of sodium nitrite on platinous diamminodichloride. Its constitution was represented:



$$\begin{array}{l} H—NO.PtCl<\begin{smallmatrix}NH_3.NH_3.NO_2\\NO_2\end{smallmatrix} \\ \quad\ \ | \\ H—NO.PtCl<\begin{smallmatrix}NH_3.NH_3.NO_2\\NO_2\end{smallmatrix} \end{array}$$

There is also **platinous diamminonitritochloronitrosylhydronitrate,**

$Pt(NH_3)_2(NO_2)Cl.NO.HNO_3$; and **platinous hexamminosulphatodihydrosulphatodinitrosylhydrosulphatodihydrochloride**, $Pt_2(NH_3)_6(HSO_4)_2SO_4.2NO.H_2SO_4.HCl$, supposed to be constituted



$$\begin{array}{l} H—NO.Pt\leqslant^{Cl}_{(NH_3)_2SO_4} \\ H—NO.Pt\leqslant^{HSO_4}_{(NH_3.NH_3.HSO_4)_2} \end{array}$$

Complex salts of platinum ammines were also made with dimethylamine, diethylamine, pyridine, and diethylsulphine.

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§ 36. Nitrogen Trioxide

E. Luck[1] found that the absorption spectrum of the so-called **nitrogen trioxide,** N_2O_3, is identical with that of nitrogen peroxide, NO_2, and he therefore inferred that nitrogen trioxide does not exist in the gaseous state. H. B. Dixon and J. D. Peterkin believed that there is a slight union when nitric oxide and nitrogen peroxide are brought into contact ; and E. Wourtzel said that with a stoichiometrical mixture of nitric oxide and nitrogen peroxide, the contraction corresponds with the formation of about 2·5 per cent. of the trioxide ; W. Ramsay and J. T. Cundall, A. Geuther, and O. N. Witt said that the yellowish-red or brown vapour produced by the evaporation of liquid nitrogen trioxide is a mixture of nitric oxide and nitrogen peroxide : $N_2O_3 \rightleftharpoons NO + NO_2$. G. Lunge, at first, maintained that the dissociation is not complete, and that nitrogen trioxide can exist as a gas even at 150° ; but later, in conjunction with G. I. Porschneff, he showed that in the gaseous state, the dissociation is virtually complete—*vide infra.* The different modes of preparation of nitrogen trioxide gas really give a mixture of nitric oxide and nitrogen peroxide which forms nitrogen trioxide only when condensed to the liquid state.

C. W. Hasenbach, and P. L. Dulong made nitrogen trioxide by passing a mixture of nitric oxide and oxygen through a heated tube. F. Birhans dried nitric oxide and oxygen by passing them separately over pumice moistened with sulphuric acid, and then over baryta and lime. The gases were then strongly cooled, and allowed to mix in a receiver cooled to —54°. One vol. of oxygen to 6–8 vols. of nitric oxide was used in order to avoid the formation of nitrogen peroxide. The trioxide thus appears as a blue liquid. L. Francesconi and N. Sciacca found that (i) liquid nitric oxide and oxygen or gaseous oxygen and liquid or solid nitric oxide, or gaseous nitric oxide and liquid oxygen, mixed in all proportions, even with the oxygen in large excess, always yield nitrogen trioxide. (ii) Gaseous nitric oxide and oxygen, the latter being in excess, also give nitrogen trioxide if they react at a temp. lower than —110°. (iii) When subjected to the action of oxygen, nitrogen trioxide is transformed into nitrogen peroxide only at temp. above —100°. (iv) The reduction of nitrogen peroxide to nitrogen trioxide by nitric oxide commences at —150°. (v) Nitrogen trioxide is stable under the ordinary pressure up to a temp. of —21°. E. Luck purified liquid nitrogen trioxide by adding ice-water until the liquid is indigo-blue ; decanting off the upper layer, and rectifying it repeatedly at 5° to 10°.

E. Péligot said that nitrogen trioxide is formed when nitric oxide is passed into liquid nitrogen peroxide. This subject has been previously discussed. N. M. Wittorff studied the fusion curves of mixtures of these two oxides, and his results are shown in Fig. 71. On saturating liquid nitrogen peroxide with nitric oxide and subsequently cooling the solution, dark blue crystals of nitrogen trioxide melting at —103° separate ; no other compound is formed. The eutectic mixture of N_2O_4 and N_2O_3 melts at —112°. It is probable

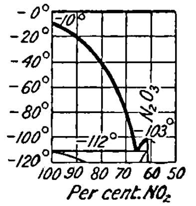


FIG. 71. — Fusion Curvo of Mixtures of Nitrogen Peroxide and Nitric Oxide.

that nitric oxide does not dissolve nitrogen trioxide. G. Baume and M. Robert found the m.p. which falls from —11·5° with 100 per cent. nitrogen peroxide to —107° with 86·3 per cent.; with 91·8 per cent. the temp. is again —107°, and with 97 per cent., —100°. According to L. S. Bagster, $5N$-HNO_3 or $6N$-HNO_3 acts on copper giving a gas with the empirical composition of nitrogen trioxide. A more conc. acid gives some nitrogen peroxide which increases proportionally with the conc. of the acid. J. Fritzsche allowed 45 parts of water to run gradually into 92 parts of nitrogen peroxide cooled to —20°; and heated the product in a retort with a receiver surrounded by a freezing mixture until the b.p. rose to 28°. C. F. Rammelsberg, and J. J. Streiff obtained a regular stream of gas by the action of water on nitroxylsulphonic acid: $HO(NO_2)SO_2+H_2O=H_2SO_4+HNO_2$; $2HNO_2=H_2O+(N_2O_3)$, which condensed to nitrogen trioxide. A similar stream of gas contaminated with other nitrogen oxides is produced by gradually dropping nitric acid on powdered glassy arsenic trioxide. G. Lunge found that with nitric acid of sp. gr. 1·20, nitric oxide is the main product; with an acid of sp. gr. 1·25, there is much nitric oxide and a little nitrogen trioxide; with an acid of sp. gr. 1·30, there is more nitrogen trioxide than nitric oxide; with an acid of sp. gr. 1·35, there is scarcely any nitric oxide mixed with the nitrogen trioxide; with an acid of sp. gr. 1·40 there is a mixture with nitrogen trioxide and peroxide in the molar proportion 100 : 126; and with an acid of sp. gr. 1·45, this proportion is 100 : 903. The reaction was also examined by A. Geuther, C. W. Hasenbach, E. Luck, C. W. G. Nylander, and O. N. Witt. A similar gas was prepared by E. Péligot, J. von Liebig, O. N. Witt, and G. Lunge by the action of nitric acid on starch. The composition of the product depends on the conc. of the acid. The last-named found that with nitric acid of sp. gr. 1·20, there is scarcely any action; with an acid of sp. gr. 1·33, the nitrogen trioxide is contaminated with a little nitric oxide; with an acid of sp. gr. 1·40, the product contains nitrogen trioxide and peroxide in the molar proportion 4 : 1; and with an acid of sp. gr. 1·50, this proportion is 5 : 3.

D. Helbig passed an electric current at 3000–4000 volts through liquid air and obtained a sky-blue powder of solid nitrogen trioxide. F. Fischer and F. Brähmer worked with an arc between platinized copper poles and obtained both nitrogen trioxide and ozone. O. Scarpa considered that in the region of the arc small amounts of oxygen and nitrogen formed by the evaporation of liquid air combine to form nitric oxide; and in the boiling air the reaction is $2NO+O=N_2O_3$. The nitrogen trioxide so produced is solid, and below its dissociation temp., so that under favourable conditions the reaction may proceed to an end. J. Fritzsche obtained a blue liquid by electrolyzing conc. nitric acid. The gas liberated by warming the blue liquid, when condensed and rectified, furnished liquid nitrogen trioxide. T. E. Thorpe and A. E. H. Tutton found that nitrogen trioxide is liberated when nitrogen peroxide is reduced by phosphorus trioxide; and D. Huizinga said that the gas is produced by the action of carbon dioxide on ammonium nitrite—though E. F. von Gorup-Besanez was unable to confirm this.

The physical properties of nitrogen trioxide.—C. W. Hasenbach said that nitrogen trioxide at —10° is an indigo-blue liquid which becomes paler as the temp. rises; and at ordinary temp., according to J. Fritzsche, the yellowish-green liquid becomes dark blue when cooled again. J. W. Mallet and R. H. Gaines found that the gas condenses to a dark green liquid when cooled to —14·4° at 755 mm. press., and if spongy platinum is present in the condensing vessel there is no perceptible difference in the temp. of liquefaction. If a very little water be present, the green liquid becomes blue; and the blue liquid does not readily mix with the green liquid. Both F. Birhans, and W. Ramsay described nitrogen trioxide at a low temp. as a blue liquid. G. Lunge and G. I. Porschneff consider the blue liquid is nitrogen trioxide, and the green one a soln. of nitric oxide in nitrogen peroxide. From observations on the thoroughly dried trioxide, B. M. Jones inferred that while liquid N_4O_6 is blue, both N_2O_3 and N_4O_6 are colourless in the gaseous state; and that ordinary liquid nitrogen trioxide is green owing to the admixture of blue N_4O_6 with a relatively large amount of moist nitrogen peroxide. The blue liquid N_2O_4 gives a brownish-red vapour, owing to the formation of NO_2 in the dissociation of the gaseous N_4O_6. At very low temp., all specimens of nitrogen trioxide, very dry or slightly wet, become quite blue. This would be due to the fact that at these temp. any "wet" NO_2 mols. would completely associate to give colourless N_2O_4 mols., which would then no longer produce a green colour with the blue N_4O_6. H. B. and M. Baker said that the liquid changes from green to indigo-blue when cooled below —2°, and that the sp. gr. of the liquid is about 1·11; but A. Geuther found the sp. gr. to be 1·4640 at —8°; 1·4555 at —4°; 1·4510 at —1°; 1·4490 at 0°; 1·4485 at 1°; and 1·4470 at 2°. E. Rabinowitsch gave 53 for the mol. vol. A. Geuther gave 3·5° for the b.p.; P. A. Guye and G. Drouginine, 2°; and C. W. Hasenbach, 2°. F. Birhans solidified the liquid at about —82°, but W. Ramsay did not freeze it at —90°. If a small quantity of nitrogen peroxide is present, the liquid freezes at —52° to —54°. D. Helbig gave —111° for the m.p.; P. A. Guye and G. Drouginine —111°; and N. M. Wittorff, —103°, see Fig. 73. D. Helbig said that when suspended in liquid air, the solid looks like green chromic hydroxide, but when the liquid air is evaporated off, the solid appears as a blue amorphous mass. N. M. Wittorff said that the solid furnishes dark blue crystals.

W. Ramsay and J. T. Cundall, and G. Lunge and G. I. Porschneff showed that the brown gas obtained by the vaporization of liquid nitrogen trioxide has a sp. gr. corresponding with that required for a mixture of nitric oxide and more or less polymerized nitrogen peroxide. The dissociation of the trioxide on vaporization is confirmed by J. Moser's observation that the spectrum of the gas is identical with that of nitrogen peroxide. L. Francesconi and N. Sciacca said that the liquid trioxide is stable at —21°; P. A. Guye and G. Drouginine found the vap. press., *p* mm., to be:

	0°	—6·2°	—10·4°	—18·1°	—20·0°	—25·2°	—80°
p . .	608	496	443	179	156	116	0

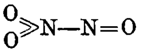
and W. Ramsay and co-workers, and G. Lunge and G. I. Porschneff found that the liquid is unstable, and can exist only in the presence of its products of dissociation. D. Gernez found that mechanical agitation favoured the decomposition of the liquid. G. Baume and M. Robert found that pure nitrogen trioxide can only exist at very low temp. in the solid state or in the liquid state under press. of nitric oxide. At temp. above —100°, it dissociates. It is not possible to distil it in a vacuum because of the immediate formation of an atmosphere of nitric oxide at temperatures at which distillation is possible. The blue liquid has no definite b.p., and by interpolation from the vap. press. curves between —80° and 35°, it is inferred that the b.p. is —27° at 760 mm. By prolonged drying over phosphorus pentoxide, H. B. and M. Baker found that the temp. could be raised to 43° before any sign of ebullition appeared. They also found that just as the dissociation of ammonium chloride does not occur if the compound be thoroughly dried, so is the dissociation of nitrogen trioxide hindered by thoroughly drying the liquid. This was shown by the vigorous absorption of the dried gas by conc. sulphuric acid, whereas an eq. mixture of nitric oxide and nitrogen peroxide is absorbed comparatively slowly. The subject was discussed by A. Smits—*vide* nitrogen peroxide.

The relative density of the gas dried for varying periods of time varied from 38·1 to 62·2. The theoretical value for undissociated nitrogen trioxide being 38, and 27·8 for dissociated nitrogen trioxide at 22°, it is therefore inferred that the dried gas contains varying amounts of polymerized nitrogen trioxide probably in the form of N_4O_6. W. Herz studied the mol. vol. Directly a minute trace of moisture is added to the nitrogen trioxide, dissociation occurs, and its density falls to about 28 at 22°. The dried liquid suffers no change of colour as it boils away, but with the moist liquid, the green colour soon changes to yellow. H. B. and M. Baker found that mol. wt. determinations of soln. nitrogen trioxide in dry benzene showed no signs of any more polymerization than is exhibited by the dried gas. The mol. wt. varied from 83 to 95—theory for N_2O_3 being 76. W. Ramsay also found the mol. wt. of ordinary nitrogen trioxide in acetic acid to be between 80·9 and 92·7. B. M. Jones found that for the dried gas, the equilibrium constant, *K*, in the reaction: $N_4O_6 \rightleftharpoons N_2O_3 + NO_2 + NO$, is:

	20°	40°	60°	80°	100°	120°	140°
K . .	513·4	144·6	46·97	15·97	5·15	2·86	0·915

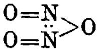
M. Berthelot gave for the heat of formation: $(N_2.3O) = -22·2$ Cals. in the gaseous state, and −8·4 Cals. in soln. J. Thomsen gave −6·82 Cals in aq. soln. B. M. Jones gave for the heat of formation of N_4O_6, 12·933 Cals. The identity of the absorption spectrum of the gas with that of nitrogen peroxide has been emphasized by W. Ramsay, and J. Moser. The spectrum was also examined by D. Brewster, E. Luck, J. N. Lockyer, W. H. Bair, and J. Chappius. H. Wieland said that nitrogen trioxide between platinum electrodes 0·1 mm. apart showed no conductivity with a potential difference of 20,000 volts. T. Soné gave $-0·21 \times 10^{-6}$ for the sp. magnetic susceptibility of liquid nitrogen trioxide which is thus diamagnetic.

The chemical properties of nitrogen trioxide.—As just indicated the analyses and mol. wt. determinations agree with the formula N_2O_3, on the assumption that a small proportion is polymerized to N_4O_6. The formula usually employed to represent the constitution is O=N—O—N=O with both nitrogen atoms tervalent. R. Günsberg suggested that one nitrogen atom is quinquevalent, and wrote:



$$\begin{matrix}O\\O\end{matrix}\!\!\geqslant N-N=O$$

This view is supported by H. Wieland, who said that the formula O : N.O.N : O is not in keeping with its intense blue colour, which is characteristic of the nitroso-derivatives, O : $N.NO_2$—*vide infra*, nitrous acid. H. Reihlen and A. Hake obtained a colourless complex with stannic chloride in carbon tetrachloride at −40°, and it is supposed to be derived from a colourless tautomeric form, O : N.O.N : O. C. D. Niven discussed the electronic structure. G. le Bas said that the molecule has the structure:



$$\begin{matrix}O=N\\O=\ddot{N}\end{matrix}\!\!>O$$

L. Francesconi and N. Sciacca, and D. Helbig showed that below −110° oxygen is without action on nitrogen trioxide, which may be preserved solid in liquid air. Above −100°, oxygen attacks the trioxide, forming nitrogen peroxide. According to G. Lunge and G. I. Porschneff, with an excess of oxygen, nitrogen trioxide is oxidized wholly to the peroxide during its evaporation. The gases, however, consist of nitrogen peroxide and nitric oxide so that the observed effect is an oxidation of the latter. The reaction was also discussed by M. Berthelot, G. Lunge, and C. W. Hasenbach. According to H. B. and M. Baker, nitrogen trioxide is insoluble in water, and forms nitric oxide and nitrogen peroxide, which dissolves in the water. As usually prepared, however, nitrogen trioxide with a little water forms a bluish-green liquid, which above 0° evolves nitric oxide, and when diluted evolves nitric oxide. E. Frémy found that in the presence of oxygen and water, nitrogen trioxide forms nitric acid. With much water, nitrogen trioxide forms nitrous acid, and it is accordingly regarded as nitrous anhydride, the parent oxide of this acid—*vide infra*. A. Sanfourche observed that nitrous anhydride, or the gaseous mixture of the same composition which reacts as the anhydride, acts on water with production of nitrous acid, which decomposes, yielding two-thirds of the original nitrogen in the form of nitric oxide. Dil. nitric acid behaves towards the anhydride in a similar manner to water, but acid of 50 per cent. and greater concentration is reduced with formation of nitrogen peroxide, which dissolves in the acid. Both reactions take place simultaneously with acids of intermediate concentrations. E. K. Rideal found that the equilibrium constant in the reaction $2HNO_3+N_2O_3 \rightleftharpoons H_2O+2N_2O_4$ at ordinary temp. is $K=0{\cdot}81$. By agitation with oxygen, the trioxide is converted into nitrogen peroxide. According to C. Weltzien, no trace of hydrogen cyanide is formed when nitrogen trioxide mixed with ethane is passed over red-hot chromic oxide. Nitrogen trioxide is absorbed by soln. of the alkali hydroxides, much more rapidly than is the case with nitrogen peroxide or nitric oxide. According to G. Klinger, the absorption is quantitative. Hence, M. le Blanc suggested that the gas really contains a little nitrogen trioxide in equilibrium with the nitric oxide and nitrogen peroxide : $N_2O_3 \rightleftharpoons NO+NO_2$; and that it is the nitrogen trioxide which is absorbed when the gas is in contact with alkali-lye. This view is supported by F. Förster, and O. Schmidt and R. Böcker. H. Wieland said that F. Raschig's observation that the trioxide is almost completely absorbed as nitrite by dil. soda-lye, when, from a completely dissociated mixture of nitric oxide and nitrogen peroxide, only the latter should react to form nitrite and nitrate while the nitric oxide remains unchanged, may be explained by assuming that nitric oxide and nitrogen peroxide carry opposite charges $N_2O_3 \rightleftharpoons NO^{\cdot}+NO'_2$, so that the $Na^{\cdot}$-ion reacts with NO'_2 and the OH'-ion with $NO^{\cdot}$, consequently, with an excess of alkali-lye, only the nitrite would be formed. This view is supported by F. Förster and A. Blich's observation that nitrogen trioxide is absorbed instantaneously by a soln. of sodium hydroxide at −22°, but liquid nitrogen peroxide is absorbed quite slowly. From the contraction which occurs on mixing nitric oxide with oxygen and with nitrogen peroxide, E. Wourtzel inferred that the gaseous mixture $N_2O_3 \rightleftharpoons NO+NO_2$ contains about 2·5 per cent. of nitrogen trioxide. F. Garelli and E. Monath observed no appreciable lowering of the f.p. of stannic chloride by the dissolution of nitrogen trioxide ; and H. Reihlen and A. Hake said that the trioxide reacts with stannic chloride, not in the ordinary blue form, but in the colourless form producing an unstable $3SnCl_4.4NO_2$.

K. A. Hofmann and A. Zedtwitz found that when mixed oxides of nitrogen, prepared from sodium nitrite and 68 per cent. nitric acid, are passed into conc. perchloric acid (a mixture of dihydrate and monohydrate), colourless, doubly refracting leaflets separate ; when these are drained and dried over phosphoric oxide in an atm. of nitrogen oxides, and finally in a vacuum, a 20–30 per cent. yield of **nitrosyl perchlorate,** $NO.O.ClO_3,H_2O$, is obtained. By evaporating the mother-liquor at 140°, and again passing nitrogen oxides, a further yield is obtained. Nitrosyl perchlorate only absorbs moisture from the air very slowly. A little water decomposes it, forming a green solution. Methyl alcohol forms methyl nitrite, and ethyl alcohol, acetone, or ether ignite with explosion. Violent explosions occur with primary aromatic amines, probably owing to the formation of diazonium perchlorates. Phenols give colorations with conc. sulphuric acid ; B. Liljensztern and L. Marchlewsky also found that nitrosyl sulphuric acid is formed. The soln. of nitrogen trioxide in chloroform was found by A. Pictet and G. Karl to react with sulphur trioxide, forming mixed anhydrides—*vide infra*. According to W. Ramsay, if nitrogen pentoxide be added to liquid nitrogen trioxide, the blue colour disappears, and liquid nitrogen peroxide is formed. A. Geuther and A. Michaelis observed that nitrogen trioxide reacts with well-cooled phosphorus trichloride, forming pyrophosphoric chloride, $P_2O_3Cl_4$, phosphorus pentoxide, phosphoryl and nitrosyl chlorides, nitrogen, and a little nitric oxide ; and with phosphorus tribromide, phosphorus pentoxide and oxychloride are formed. H. B. and M. Baker found that dry nitrogen trioxide does not react with dry benzene. Many reactions of nitrogen trioxide are discussed in connection with nitrous acid. F. Kuhlmann reported the formation of *stannic nitrochloride,* $SnCl_4.N_2O_3$, as a non-crystalline, orange-yellow mass by the action of dry nitrogen trioxide on stannic chloride, but the product is thought by R. Weber, and W. Hampe to be a nitrosyl complex, $SnCl_4.2NOCl$.

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§ 37. Nitrous Acid

In 1774, C. W. Scheele[1] in his memoir: *De magnesia nigra*, showed that when potassium nitrate is kept in a state of fusion for half an hour at a red-heat, "it acquires phlogiston"; otherwise expressed, it loses oxygen, or is reduced. The acid contained in the salt is quite different from what it was before the fusion. The product "deliquesces in air although there is no evidence of any superabundant alkali." The new acid in the ignited nitre is so feeble, said T. Bergman, that it can be displaced by vinegar, and he called it *phlogisticated nitric acid*. In 1772, J. Priestley observed the different colours assumed when nitric acid is treated with nitric oxide, and found that the colour which is at first orange-yellow finally becomes a blue or green, forming what was later shown to be the phlogisticated nitric acid. These facts were not appreciated until J. J. Berzelius had demonstrated that there are at least two definite acids concerned in these reactions—nitrous acid, and nitric acid—and he established the fact that nitrous acid is a specific acid which forms with the saline bases a series of salts—the nitrites—with properties quite distinct from those of the nitrates. In 1802, J. L. Proust concluded from his observations on the action of lead on a boiling soln. of lead nitrate that the yellow crystals obtained represented a salt of lead in a lower state of oxidation; but J. J. Berzelius' observations showed that the yellow crystals were a nitrite and not a nitrate of lead. Similar results were obtained by the action of silver on silver nitrate. The additional observations of J. L. Gay Lussac,[2] and of P. L. Dulong in 1816, and the work of E. Péligot in 1841, proved that while nitric acid has the composition HNO_3, nitrous acid has the composition HNO_2. The name **nitrous acid** recommended by R. Chenevix is used at the present day, and the salts of the acid are called **nitrites.**

The occurrence of nitrous acid and nitrites in atm. air has already been discussed. The air of the best ventilated rooms where gas is burnt contains nitrites. L. I. de Nagy Ilosva found that nitrites are exhaled from the lungs in breathing, and C. Wurster, and T. Cramer believe that the depressed feeling and uneasiness experienced in crowded rooms is due to the presence of nitrites. J. Chabrier found from 0·75 to 4·52 mgrm. N_2O_3 per kgrm. in many soils. The presence of nitrites in soils has been treated by C. F. Schönbein, L. Carius, A. Houzeau, F. A. Haarstick, A. Müntz and T. Schlösing, R. Warington, L. Spiegel, E. Schaer, F. H. Storer, S. W. Johnson, etc.—*vide* the fixation of nitrogen. J. Chabrier also found nitrites in saltpetre prepared artificially; E. Bödtker found small traces of nitrites in sea-water; and J. E. Enklaar, in ordinary water. The presence of nitrites in spittle was detected by R. Böttger, C. Wurster, P. Griess, and R. N. Musgrave. The last-named found 0·4 to 2·0 parts of nitrous acid per million. The presence of nitrites in urine was discussed by C. F. Schönbein, F. Goppelsröder, H. B. Jones, and C. Jaffé. H. Struve found ammonium nitrite in expired air. G. Bertoni and C. Raimondi found nitrites in blood after poisoning with hydroxylamine. C. F. Schönbein, and P. Genadius found nitrites in the juices of some plants—*Boletus luridus, Leontodon taraxacum, Spinacia oberacea,* etc.

The preparation of nitrous acid and the nitrites.—Nitrous acid is found in the blue solution formed when nitrogen trioxide, N_2O_3, is dissolved in cold water: $N_2O_3+H_2O=2HNO_2$; and a mixture of nitrous and nitric acids is formed when nitrogen peroxide, N_2O_4, is dissolved in water: $N_2O_4+H_2O=HNO_2+HNO_3$. This acid is formed, according to D. Waldie, when a mixture of hydrogen and nitric oxide is burnt in air. Nitrous acid, however, is so unstable that it is usually studied when combined with the bases in the form of salts. Pure nitrous acid has not been isolated. A soln. of nitrous acid can be made by adding hydrochloric or sulphuric acid or acetic acid to a soln. of the nitrite: $NaNO_2+HCl=NaCl+HNO_2$. Some nitric oxide and nitric acid may be formed at the same time. According to C. W. Hasenbach, and J. Fritzsche, if nitrogen trioxide be passed into water, at 0°, a blue liquid is formed. The aq. soln. of the acid at low temp.—say −10°—is an indigo-blue colour which becomes yellowish-green at room temp.; the blue colour returns on re-cooling the soln., but it is rather paler than before owing to loss by decomposition. If the temp. be higher than this, nitric oxide is evolved, and nitric acid is formed: $3N_2O_3+H_2O=4NO+2HNO_3$. E. Frémy found that nitrogen trioxide, with a little water, forms nitric oxide and nitric acid, but with much water, the soln. does not decompose and is fairly stable. H. Reinsch considered that in cold water, nitrogen trioxide forms hydrated nitrous acid; and since an aq. soln. prepared out of contact with air conducts electricity, L. Marchlewsky inferred that a hydrated nitrous acid is present. H. Reinsch also found that an aq. soln. of nitrogen peroxide contains some nitrous as well as nitric acid. A. V. Saposchnikoff found aq. soln. of nitrous acid to be stable below 0°; but could not obtain a constant value for the distribution of nitrous acid between water and chloroform.

(1) *By the action of nitrogen oxides on alkaline hydroxides*—*vide* E. Turpin.—J. L. Gay Lussac, P. L. Dulong, J. Fritzsche, F. Emich, M. Berthelot, and T. Thomson found that a mixture of oxygen and a large excess of nitric oxide, say (1 : 4), in contact with a soln. of potash-lye forms potassium nitrite; and E. Péligot said that when nitric oxide comes in contact with mercurous oxide, mercurous nitrite is formed. C. F. Schönbein, and P. Sabatier and J. B. Senderens obtained nitrites by the action of nitric oxide on barium dioxide; C. F. Schönbein, on hydrogen dioxide, or manganese dioxide, or silver oxide. The nitrites are formed when nitrogen trioxide or nitrogen peroxide is passed into a soln. of potassium or sodium

hydroxide. With nitrogen peroxide, the corresponding nitrate is formed at the same time as the nitrite, and the two can be more or less cleanly separated by fractional crystallization; if the nitrogen trioxide is mixed with a slight excess of nitric oxide, NO, very little nitrate is formed. Commercially, the nitrous fumes obtained by passing an electric discharge in air (*vide supra*) at a temp. of about 300° are passed into the alkali-lye, and fairly pure nitrite is formed. The nitric oxide formed by the electric discharge does not oxidize further than N_2O_3 when the temp. does not fall below 300°.

(2) *By the reduction of the fused nitrates or their aqueous solutions.*—B. Moore found that ordinary tap-water which has stood for a day in darkness contains no nitrites, but if it has been exposed to the sun for an hour or two, nitrites are formed. Nitrates are thus reduced to nitrites when exposed to sunlight. Ordinary running water, or dew, may contain nitrites for a similar reason. According to S. Cooke, dil. nitric acid in the presence of spongy platinum is reduced by hydrogen with the formation of ammonium nitrite. J. J. Berzelius showed that when a soln. of lead nitrite is boiled with lead, the latter is oxidized at the expense of the nitrate, and lead nitrite is formed. C. F. Schönbein obtained it by reducing aq. soln. of the nitrates or nitric acid by stirring them with a cadmium or zinc rod, or by the addition of potassium-, sodium-, lead-, or zinc-amalgam—but not of iron-, aluminium-, or tin-amalgam; E. Müller and J. Weber, by the electrolysis of a soln. of a nitrate with silver or copper electrodes when the nitrate is almost wholly reduced to the nitrite before the latter commences to be reduced to ammonia. F. Gantter obtained nitrites by reducing nitrates by phosphorous acid; G. Flick, by the action of sulphur dioxide in the presence of lime which fixes the sulphuric acid simultaneously formed: $NaNO_3+CaO+SO_2=CaSO_4+NaNO_2$; G. Arth, and E. Divers, by the action of zinc, iron, etc., on the product of the action of ammonia on ammonium nitrate; H. Morin, by the action of cadmium on a soln. of ammonium nitrate; M. Goldschmidt, by the reducing action of carbon monoxide, formic acid or the formates; and J. Priestley, and J. L. Gay Lussac, by passing nitric oxide into nitric acid. V. H. Veley showed that the reaction between nitric oxide and nitric acid: $2NO+HNO_3+H_2O\rightleftharpoons3HNO_2$, is reversible, when the soln. is sufficiently dil. and the temp. low. For equilibrium, the ratio of the quantities of nitric acids is about 9 : 1. With more conc. acids, and at higher temp., the chemical changes taking place are more complicated. In soln. containing both nitric and nitrous acids, the rate of change at any moment is proportional to the mass of the nitrous acid present, and is dependent on the ratio of the masses of nitrous and nitric acid, being the more rapid the greater the proportion of the former to that of the latter. In the particular case of the liquids prepared from nitric oxide and nitric acid, the rate of change was found to vary with the temp. according to the equation $v_t=vk^{t-t_1}$. Nitrous-nitric acid soln. prepared in different ways behave in a similar manner as regards the diminution of the mass of the nitrous acid, but in other respects, such as the evolution of gases and action on metals, they are dissimilar. E. Divers showed that nitrites as well as nitrates are formed when the metals (*q.v.*) copper, silver, mercury, and bismuth are dissolved in nitric acid, but only nitrates and ammonia, or hydroxylamine, are formed when the alkali metals, magnesium, zinc, cadmium, aluminium, tin, lead, and iron, are similarly treated. The subject is discussed in connection with specific metals—*e.g.* copper. According to W. J. Russell, E. Divers, and V. H. Veley, many metals dissolve in nitric acid only when nitrous acid is present, and this has been attributed to the formation of nitrites which are attacked by the nitric acid, or else to the nitrous acid acting as a depolarizer. W. D. Bancroft holds that the nitrous acid acts catalytically to activate the nitric acid, possibly through the dynamic equilibrium: $3HNO_2\rightleftharpoons HNO_3+2NO+H_2O$. As already indicated, it was known in the middle of the eighteenth century that sodium or potassium nitrate decomposes when heated, forming a new salt, which was later shown to be the alkali nitrite. N. W. Fischer recognized that the reaction is difficult to control, and he found that better results

are obtained if the molten nitrate be treated with hydrogen, or preferably mixed with a reducing agent like charcoal, or lead. Thus, when a mixture of lead filings and an equal weight of sodium nitrate is heated in a crucible to about 420°, oxygen is slowly transferred from the nitrate to the lead; the main reaction is represented: $3Pb+4NaNO_3=Pb_3O_4+4NaNO_2$, or $Pb+NaNO_3=PbO+NaNO_2$. The temp. developed during the reaction is not sufficient to decompose much of the nitrite to sodium oxide—indeed, a 90 per cent. yield of nitrite can be formed under manufacturing conditions. The fused mass is digested with water, filtered, and the soln. evaporated when a crop of crystals of sodium nitrite separates on cooling. The lead oxide can be recovered and sold as litharge, while the unconverted lead can be recovered and used over again. J. Milbauer and O. Vogel said that the reaction $Pb+NaNO_3=NaNO_2+PbO$ proceeds completely to the right if a 15 per cent. excess of lead is employed, at about a hundred degrees above the m.p. of sodium nitrate—*viz.* 315°. The yield of lead oxide is less than the theoretical because of the dissociation of the nitrate into nitrite and oxygen. G. Tacchini recommended heating sodium nitrate with barium oxide or manganese dioxide. Several reducing agents have been recommended—thus, G. A. le Roy employed barium or calcium sulphide; A. Étard, alkali sulphite; and L. G. Paul, sodium hydroxide and sulphur—either the yield of nitrite is not so good as with lead, or the resulting nitrite is not so readily freed from impurities—sulphates, etc.—formed during the reaction. Nitrates were produced by E. Müller and co-workers, J. Weber, and W. J. Müller by the electro-reduction of nitrates.

(3) *By the reduction of nitric acid.*—E. Abel and D. Harasty studied the reaction: $HNO_3+H_2O+2NO=3HNO_2$, which occurs when nitric oxide is bubbled through nitric acid—*vide supra*, nitric oxide; and *infra* for the reverse reaction. The reaction is heterogeneous (the velocity of reduction is decreased by decreasing the glass surface of the apparatus) and is autocatalyzed by the nitrous acid, which acts as a superposed positive and negative catalyst; it accelerates the reduction when its conc. is small and retards it as the conc. becomes larger. The velocity increases with increasing velocity of the nitric oxide stream and with decreasing vol. of the soln. of the reactants. The latter effect is mainly due to change in the hydrogen-ion conc. of the nitric acid; the nitrate-ion conc. has only a small influence. Sodium sulphate retards the reaction and in moderately large conc. practically stops it. J. H. Gladstone and A. Tribe, and E. Müller and J. Weber found that nitrous acid is the first reduction product of nitric acid. According to K. Boresch, certain insoluble ferruginous substances—*e.g.* finely powdered ferromagnesian minerals, iron ores, and basic slag—can reduce neutral, aq. soln. of nitrates to nitrites. The reduction is favoured by the presence of ammonium salts which are themselves oxidized to nitrites. The ferrous oxide appears to act as a catalyst. The formation of nitrites from nitrates and ammonium salts is an incomplete bimolecular reaction. Only an insignificant amount of nitrite is formed by the action of manganese compounds. These reactions play a part in the changes suffered by nitrogenous compounds in soils.

(4) *By the oxidation of nitrogen, ammonia, and nitrogen-hydrogen compounds.*—C. F. Schönbein, O. Löw, and M. Zabelin said that ammonium nitrite is formed when water is evaporated or distilled in air; R. Warington found that nitrites are produced during the evaporation of water in vessels exposed to air, but not in closed vessels; and A. von Lösecke said that the amount produced is greater the lower the temp. On the other hand, L. Carius, E. Bohlig, P. Freda, and N. Smith failed to confirm the observation when care is taken to use air free from nitrites. According to C. F. Schönbein, P. Zöller and E. A. Grete, H. Struve, A. W. Hofmann, M. Zabelin, O. Löw, H. B. Jones, H. Kolbe, R. Böttger, J. D. Boeke, A. R. Leeds, L. T. Wright, C. Than, and L. I. de Nagy Ilosva, nitrous acid or ammonium nitrite is formed in traces when hydrogen, coal, carbon monoxide, wax, coal-gas, alcohol, and various hydrocarbons are burnt in air, and, added F. Fischer and F. Brähmer, this occurs even when the temp. is very low, for nitrous acid is

produced by the combustion of carbon monoxide, acetylene, carbon, wood, and sulphur in liquid air—*vide supra,* fixation of nitrogen. C. F. Schönbein, M. Berthelot, M. Zabelin, and G. Meissner reported on the production of nitrites during the slow oxidation of phosphorus in air; S. Kappel, by passing air over magnesium in contact with potassium hydroxide; E. Reichardt, by shaking water with manganic hydroxide and magnesium carbonate—but P. Zöller and E. A. Grete could not confirm this; A. A. Bonnema, by shaking ferric hydroxide in air—but F. Sestini denied this; M. Berthelot, and R. Pohl, by sparking a mixture of nitrogen and steam obtained ammonium nitrite, and S. M. Losanitsch and M. Z. Jovitschitsch obtained a similar result by the silent discharge. L. I. de Nagy Ilosva observed the formation of nitrous acid when a current of air is passed over reduced iron at 190°–250°.

The oxidation of ammonia has been previously discussed. O. Löw, L. T. Wright, and H. N. Warren observed the formation of ammonium nitrite when ammonia and air are passed over warm platinized asbestos. C. F. Schönbein, and S. Kappel obtained a similar result with reduced copper, nickel, or iron. F. Sestini said that ferric hydroxide can oxidize ammonia to the nitrite. When copper is oxidized in the presence of ammonia, the latter is simultaneously oxidized to a nitrite; this reaction was examined by C. F. Schönbein, E. Péligot, M. Berthelot and L. P. de St. Gilles, and D. K. Tuttle. C. F. Schönbein, and C. Kraut observed the formation of nitrites when a spiral of platinum, copper, or nickel wire is heated in ammoniacal air. According to F. Bayer, nitrous acid and not nitric acid is formed when a mixture of air or oxygen and ammonia is passed over ferric oxide or copper oxide at a temp. exceeding 650°. C. F. Schönbein obtained ammonium nitrite by passing electric sparks through aq. ammonia in the presence of air. C. F. Böhringer, and C. Couchet and co-workers reduced nitrates to nitrites by the electrolysis of aq. soln. with a mercury cathode. A nitrite is formed by the electrolysis of a soln. of ammonia in soda-lye in the presence of cupric hydroxide, and W. Traube and A. Biltz using a current of 5–15 amps., and platinum or iron electrodes, showed that virtually all the anode oxygen is used in oxidizing the ammonia to nitrite before the latter is converted into nitrate. E. Müller and F. Spitzer studied the nature of the anode material on the electro-reduction of nitrates to nitrites. According to C. F. Schönbein, aq. ammonia is oxidized to the nitrite by hydrogen dioxide, and by potassium permanganate, particularly when agitated in the presence of platinum-black, and the reaction was found by L. P. de St. Gilles to be quicker in the presence of formic acid. The reaction was investigated by F. Wöhler, W. Weith and R. Weber, F. Hoppe-Seyler, and H. Tamm. Various organic compounds were found by E. Donath to be energetically oxidized to nitrous acid by treatment with potassium permanganate. C. M. Tessié du Motay found that a mixture of oxygen and ammonia is oxidized to nitrite, nitrate, or free nitric acid when passed over lead manganate, permanganate, or dichromate at 350°–550°.

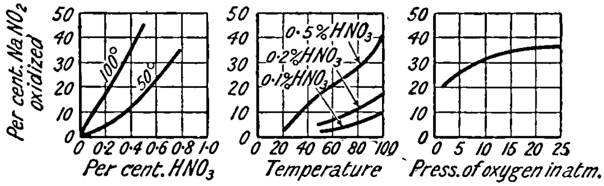
(5) *Biological processes.*—Nitrites are formed during the putrefaction and decay of nitrogenous substances. The oxidation of ammonia by bacteria has been discussed in connection with the fixation of nitrogen. Observations on the subject were made by C. F. Schönbein, F. Schür, P. F. Frankland and co-workers, E. Laurent, T. Schlösing, T. Leone, A. Müntz, S. Winogradsky, etc. The reverse action, *denitrification* of nitrates by bacteria, whereby nitrites are formed was probably observed by C. F. Schönbein in 1868; and the subject has been discussed by O. Baudische, E. Baur, M. W. Beyerinck, P. A. Boncquet, F. Bordas and co-co-workers, H. von Caron, J. Chukevich, M. Chwilewsky, E. Crespolani, A. Dieudonné, F. Duchacek, P. F. Frankland, U. Gayon and G. Dupetit, V. Griessmayer, L. Grimbert and L. Ficquet, C. A. Herter, B. Horowitz, H. Jensen, A. Jorissen, M. Klaeser, H. Kühl, E. Laurent, W. T. Logie, M. Lunkewitsch, A. Maassen, P. Mazé, L. Mazzetti, E. Meusel, E. Müller and F. Spitzer, E. Pelz, R. J. Petri, W. Seifert, A. Springer, J. Stoklasa, W. B. Wherry, etc. *Vide infra* for the reduction to ammonia and nitrogen.

The properties of nitrous acid and the nitrites.—The aq. soln. of the alkali nitrites were found by J. J. Berzelius to decompose slowly in boiling: $3KNO_2+H_2O=KNO_3+2KOH+2NO$—*vide infra* for ammonium salts. The aq. soln. when boiled in air, were also found to absorb oxygen, so as to form nitrates. G. Lunge showed that aq. soln. slowly pass into nitrates. According to E. Frémy, the aq. soln. at 0° is fairly stable, above that temp. it decomposes if in conc. soln. Indifferent powders like sand, gypsum, and charcoal accelerate the decomposition. A. V. Saposchnikoff found aq. soln. of nitrous acid to be stable below 0°; but he could not obtain a constant value for the distribution of nitrous acid between water and chloroform. According to C. Montemartini, an aq. soln. of the acid decomposes according to the rule for unimolecular processes, and judging by the final products, the simplest equation: $3HNO_2 \rightleftharpoons 2NO+HNO_3+H_2O$, is a termolecular process. This shows that the decomposition involves at least two operations—a slow unimolecular process and an immeasurably quicker process. The reaction is probably reversible because it is hindered in a marked way by increasing the press. of the nitric oxide. A. V. Saposchnikoff represented the velocity of the reaction by $K=(1/x_t) \log \{x_t(a-x)/a(x_t-x)\}$, where a denotes the initial conc. of the nitrous acid; x_t, the conc. at the time t; and x, the conc. after 300 hrs. when the soln. has been agitated energetically. He found that for nitric acid varying from N- to ^{1}N-conc., the equilibrium constant is 159; and for $0{\cdot}05N$-HNO_3, 232; this is taken to indicate that with low conc., the reaction proceeds very slowly and does not reach a final stage of equilibrium. G. N. Lewis and A. Edgar found for the equilibrium constant $K=[HNO_2]^3/[H^{\cdot}][NO'_3]$, in the reaction $3HNO_2 \rightleftharpoons 2NO+H_2O+H^{\cdot}+NO'_3$ to be $K=0{\cdot}0267$ at 25°; A. V. Saposchnikoff's value 0·0175 becomes 0·0208 if the same data are employed in the two cases. The water is assumed to be constant, and the nitric oxide being always present at the same press. is also constant. P. C. Ray, M. L. Dey and J. C. Ghosh found that the measurements of the rate of decomposition agree with those required for a unimolecular change, and the velocity coeff. at 0°, 21°, and 40° are respectively 0·00014, 0·00022, and 0·00057. A. Klemenc and F. Pollak showed that the decomposition $3HNO_2=HNO_3+2NO+H_2O$ depends on the velocity at which nitric oxide is removed from the soln. Undissociated nitrous acid possesses a considerable press. of nitric oxide, and, in consequence, the velocity of decomposition is proportional to the conc. of undissociated nitrous acid. The conc. of free nitric oxide in aq. soln. may be regarded as approximately the same as that of the undissociated nitrous acid. When nitrogen, or another inert gas, is led through a soln. of nitrous acid the velocity of decomposition is increased, and the velocity constant increases with the increasing rate at which the nitrogen is passed through. The speed of the direct decomposition of nitrous acid is in all probability immeasurably rapid. Nitrous acid decomposes spontaneously into nitric oxide, and the hydroxyl radicle and its transitory existence in aq. soln. is due to a mutual action between it and the solvent. The presence of mineral acids increases the velocity of decomposition. V. H. Veley showed that the reaction is probably reversible, and A. V. Saposchnikoff showed that the reverse change is very slow with dil. soln. of nitric acid. According to T. W. J. Taylor and co-workers, the reaction is at first rapid, and it subsequently slows down. If the nitrous acid be mixed with sodium sulphate, and kept under a layer of paraffin, the decomposition is considerably retarded. The first stage of the decomposition is represented by a state of equilibrium: $2HNO_2 \rightleftharpoons N_2O_3+H_2O$, and the complicated nature of the subsequent changes arises from the behaviour of the anhydride; that this latter exists in soln. is supported by the observations of A. V. Saposchnikoff on the ease with which organic solvents will dissolve it from soln. of the acid. It is not the anhydride itself which escapes as gas from the soln., for, if this were so, the soln. would contain eventually less nitric acid than the quantity corresponding to the equation of decomposition: $3HNO_3=HNO_2+2NO+H_2O$, and experiment showed that in every case under paraffin the theoretical amount of nitric acid remained. The facts are explained by the assumption that another state of equilibrium exists, namely, $N_2O_3 \rightleftharpoons NO + NO_2$. In a completely stable soln., the conc. of water being assumed to be constant, the function $[NO][NO_2]/[HNO_2]^2$ would have a fixed value at any one temp.; but the conc. of nitric oxide cannot exceed a certain limit because of its slight solubility, and the limit will depend on the press. No completely stable soln., however, can exist, even in a sealed bulb where the press. of nitric oxide can become high, since the nitrogen peroxide is continually hydrated and removed from the equilibrium. During the "slow" decomposition of the nitrous acid, two factors come into play: the rate of escape of nitric oxide, and the rate of hydration of the peroxide. The conc. of the latter is probably extremely small, and thus the quantity hydrated in unit time is small, and consequently the second factor under normal conditions is of less importance. Any factor tending to facilitate the escape of the nitric oxide, such as increased area of contact with the gas phase, addition of sand or charcoal or reduction of press., will increase the rate of decomposition.

N. R. Dhar showed that the decomposition of nitrous acid into nitric acid and nitric oxide is hindered by mild reducing agents; and K. B. Mukerji and N. R. Dhar, that the velocity coeff. in both the light and the dark increases slowly with increase of conc. of the nitrous acid. The velocity coeff. are considerably greater—from 200 to 400 per cent.—when the reaction is carried out in open vessels than when closed vessels are employed. This is attributed to a displacement of equilibrium owing to the removal of nitric oxide under the former conditions. The velocity of the reaction is markedly accelerated by light, and to a greater extent when closed vessels are used. The following substances act as positive catalysts for the reaction: ferric nitrate, cobalt nitrate, nickel nitrate, chromium chloride, copper sulphate, nitric acid, potassium chlorate, potassium nitrate, sulphuric acid, ferric hydroxide sol, molybdic and titanic acids, bromocamphor, thiocarbamide, dinitrophenol, carbamide, phthalic anhydride, citric, tartaric, and formic acids, potassium oxalate, potassium formate, boric acid, and tartar emetic. The following act as negative catalysts: sucrose, dextrose, glycerol, alcohol, hydrogen dioxide, ethyl ether, quinol, phenol, brucine, strychnine, narcotine, and quinine sulphate. Manganese nitrate and barium sulphate are without effect. The results indicate that reducing agents retard reactions involving auto-oxidation and reduction processes. The subject was also investigated by V. H. Veley, A. Jacob, J. Knox and D. M. Reid, and R. Abegg and H. Pick. A. Jacob found that the first stage of the reaction is probably $2HNO_3 = H_2O + N_2O_3$. According to J. Thomsen, the heat of formation (2N,3O,aq.) is $-6{\cdot}82$ Cals.; (2NO,O,aq.), $-36{\cdot}33$ Cals.; $(H,N,O_2,aq.)+30{\cdot}77$ Cals.; and $(NO,O,H,aq.)+52{\cdot}35$ Cals. M. Berthelot gave 9·1 Cals. for the heat of neutralization with ammonia; and 10·6 Cals. with baryta. A. Jacob calculated for the reaction $3HNO_2aq. \rightleftharpoons HNO_3aq. + 2NO + H_2O - 17{,}900$ cals. From the conductivity of the mercury salt, H. Ley and H. Kissel concluded that nitrous acid is rather stronger than acetic acid—*vide infra*, silver nitrite.

A. A. Blanchard calculated from the effect of carbon dioxide on soln. of potassium nitrite the ionization constant, $K=[H^{\cdot}][NO'_2]/[HNO_2]$, to be 0·00040; M. Schümann gave 0·00045; P. C. Ray and co-workers, 0·00060 at 0°; and E. Bauer, 0·00064. C. Matignon and G. Gire found that the electrical conductivity and the progressive displacement of nitrous acid by sulphuric in a dil. soln. of sodium nitrite indicate that nitrous acid is a stronger acid than the second acid function of phosphoric acid—the ionization constant for nitrous acid is 6×10^{-4}, and for the second acid function of phosphoric acid, $1{\cdot}9\times10^{-7}$. They also examined the effect of different indicators. E. Bauer found the transport number of the NO'_2-ions to be 58; M. Schümann gave 64·5; H. Pick, 63; N. R. Dhar and D. N. Bhattacharyya, 67·9 at 25° and infinite dilution; S. von Niementowsky and J. von Roszkowsky, 72·3 (when that for NO'_3-ion is 65·1); and F. Vogel, 61·7. According to R. Abegg and H. Pick, when heated in a closed vessel above 40°, soln. of silver nitrite were decomposed according to the equation $2AgNO_2 \rightleftharpoons Ag + NO + AgNO_3$, or, on the ionic theory, $2Ag^{\cdot} + 2NO'_2 \rightleftharpoons Ag + Ag + NO + NO'_3$; the action is a reversible one. If p denotes the partial press. of the nitric oxide, the constant $k=p[NO'_3]/[Ag^{\cdot}][NO'_2]^2$ has the value $1{\cdot}9\times10^5$ at 55°, the pressure of nitric oxide being expressed in atm. and the conc. of the other substances in mols. per litre. From this it is calculated that the intensity of the oxidation reaction $2NO'_2\rightarrow NO+NO'_3$ is $-0{\cdot}43$ volt, the potential of the hydrogen electrode being taken as zero; in other words, when the substances taking part in the equilibrium are present in unit concentration, the nitrite ion is, by 0·43 volt, a less powerful reducing agent than hydrogen, but the reducing action of the former is greatly increased when the nitric oxide conc. is small. According to R. Ihle, if the oxidation of the hydrogen ions in a Grove's cell is not sufficiently rapid, polarization occurs, and the e.m.f. falls considerably. This oxidation velocity is largely dependent on the conc. of the acid, and is increased by the addition of small quantities of nitrous acid. Thus, although polarization with a pure acid occurred when the conc. was 35 per cent., by the addition of 5 drops of nitrite soln. the acid could be further diluted to 20 per cent. without any polarization. Owing to this action of nitrous acid, urea and strong oxidizing agents, such as potassium permanganate, have a retarding effect on the oxidation velocity, which may further be increased by some reducing agents. The potential of the nitric acid increases with the conc., the values 1·23 volt, at 6 per cent., and 1·52 volt, at 95·5 per cent., being obtained. Nitrous acid, however, lowers the potential, and its effect in this respect was found to be a logarithmic function of its conc. The potential of nitrous acid itself was found to be lower than that of nitric acid. It was inferred that nitrous acid is the real depolarizer in Grove's cell. H. Pick, and A. Klemenc and P. Gross studied the anodic behaviour of nitrous acid. A. Klemenc showed that when a platinum electrode is in contact with the system: HNO_2–HNO_3–NO, in equilibrium, the reaction in approximately 3*N*-soln. is $NO+2H_2O\rightarrow4H^{\cdot}+NO'_3$; but in more dil. soln., the reaction: $NO+H_2O\rightarrow2H^{\cdot}+NO'_2$ also comes into play.

According to L. I. de Nagy Ilosva, nitrous acid can act both as an oxidizing and as a reducing agent. Thus it has a *reducing action* when it is oxidized to nitric acid—*e.g.* when treated with ozone or hydrogen dioxide, and in the latter case, added C. F. Schönbein, sunlight accelerates the change. K. B. Mukerji and N. R. Dhar estimated that the photochemical action of light persisted only $4{\cdot}2\times10^{-9}$ secs. M. Busch said the oxidation with hydrogen dioxide is complete in acid soln. The reactions were also studied by W. Weith and R. Weber, A. Perrot, R. Böttger, and H. Buff and A. W. Hofmann after exposure. C. F. Schönbein found that nitrous acid also reduces lead or manganese dioxide, and the brown soln. of silver dioxide in cold nitric acid. H. Zieler examined the oxidation of sodium nitrite or nitrous acid. Since the oxidizing action of nitric acid usually ceases when it has been reduced to nitric oxide; and the reaction: $4NO+3O_2+2H_2O=4HNO_3$ involves a decrease in vol., oxidations can be effected by oxygen under press. with nitric acid as catalytic agent. Thus, while neutral soln. of sodium nitrite are not oxidized by oxygen under a press. of 20 atm., in soln. acidified by nitric acid, the oxidation to nitrate is quantitative. The rate of oxidation increases with increase in the acidity, with the dilution of the soln., with the temp., and to a less extent with oxygen press. The results are summarized in Figs. 72 to 74—*vide infra*, sodium nitrite. A. W. Francis studied the speed of oxidation of sodium nitrite by bromine-water. R. C. Banerji and N. R. Dhar found that the reaction with iodine is bimolecular: $NaNO_2+I_2+H_2O=NaNO_3+2HI$, in darkness,



FIGS. 72 to 74.—The Effect of the Concentration of Nitric Acid, the Temperature, and the Pressure of the Oxygen on the Oxidation of Nitrous Acid or Sodium Nitrite.

but in light, the semimolecular formula gives better results for the velocity constant for the consumption of iodine. N. A. E. Millon said that chloric acid is reduced to chlorous acid, and H. Toussaint reduced it to hydrochloric acid. A. Schwicker, and W. Feit and K. Kubierschky found that it reduces bromic acid to bromine, forming nitric acid, but iodic acid, on the other hand, is not attacked in cold, conc. soln. A. Kurtenacker examined the velocity of the reduction of iodic acid by nitrous acid, and found that the reaction is best represented as occurring in two stages: (i) $IO'_3+2NO'_2=IO'+2NO'_3$; and (ii) $2IO'+NO'_2+2H^{\cdot}=I_2+NO'_3+H_2O$. The velocity of the second reaction is much less than that of the first. There may possibly be three stages (i) $IO'_3+NO'_2=IO'_2+NO'_3$; (ii) $IO'_2+NO'_2=IO'+NO'_3$; and (iii) $2IO'+NO'_2+2H^{\cdot}=I_2+NO'_3+H_2O$. The velocity of reduction of the iodate is found to be directly proportional to the conc. of the iodate, nitrite, and hydrogen ions, and is catalytically accelerated by the hypoiodous acid formed in the reaction. In the presence of potassium chloride, bromide, and nitrate, the nitrate ion slightly retards the velocity of reduction of the iodate, whilst the presence of chlorine or bromine ions exerts a marked accelerating effect, the influence of the bromine ion being about twenty times greater than that of the chlorine ion. For small conc. the catalytic action of the halogen ions is directly proportional to their conc.; with large conc., however, the accelerating influence falls off, owing to the conversion of hypoiodous acid into iodine monochloride or monobromide, which exert no catalytic action on the reduction of the iodate. The reaction with bromic acid occurs in three stages: (i) $BrO'_3+3NO'_2=Br+3NO_3$; (ii) $BrO'_3+5Br'+6H^{\cdot}=3Br_2+3H_2O$; and (iii) $Br_2+NO'_2+H_2O=2Br'+NO'_3+2H^{\cdot}$. The reaction is of the first order with respect to the bromate. The reaction is very slightly influenced by the conc. of the nitrite, and only when the relation of the conc. of bromate to nitrite is very large or equal to unity. With large conc. of nitrite the velocity is independent of the nitrite conc., and in this case the reaction is of the first order. The velocity is strongly accelerated by acetic acid. The behaviour of the nitrite and the acetic acid is explained by the assumption that the reaction which has been measured consists in the interaction of bromic acid, and nitric oxide, and in which the nitrous acid is only so far active as it produces the nitric oxide as fast as it is used up. Consequently, it is very probable that the first stage proceeds (i*a*) $3NO'_2+2H^{\cdot}=2NO+NO'_3+H_2O$; and (i*b*) $BrO'_3+2NO+H_2O=Br'+2NO'_3+2H^{\cdot}$. Diminution of press. decreases the reaction velocity, owing to decrease in conc. of nitric oxide. The extent of the decrease is scarcely so great as would be expected, possibly owing to an increased instability of nitrous acid, due to the lower press. The effect of temp. on the velocity of the reaction is that which would be expected if oxidation affects the nitric oxide. The reaction with chloric acid, in the presence of potassium hydrosulphate, can be expressed by the formula $dx/dt=(K_1+K_2S)[ClO'_3][HNO_2]$, where K_1 is the velocity coeff. of the uncatalyzed action, K_2 the acceleration coeff. of the acid, and S the conc. of the latter. Very marked differences are found in the mechanism of the action with chloric, bromic, and iodic acids respectively; the greatest abnormality is observed with bromic acid, which, in contrast with its position in the natural series, acts much more rapidly than either chloric or iodic acid. C. F. Schönbein, E. Frémy, L. P. de St. Gilles, and W. Kubel reduced permanganates in the presence of sulphuric acid with the formation of manganese sulphate: $2KMnO_4+5HNO_2+3H_2SO_4=K_2SO_4+2MnSO_4+5HNO_3+3H_2O$. In volumetric analyses, where the nitrite is titrated with standard permanganate, in order to avoid a decomposition of the nitric acid by the sulphuric acid, it is necessary to use a dil. soln. containing at least 5000 parts of water for one of nitric acid. Hence, L. P. de St. Gilles determined nitrites in dil. acid soln. by titration with permanganate. A. Kurtenacker found that the speed of reduction of permanganate by nitrous acid is greater than in the case of dichromates, chlorates, bromates, or iodates. G. A. Barbieri reduced ceric sulphate, $Ce(SO_4)_2$, quantitatively with nitrous acid; and L. L. de Koninck, potassium chromate or dichromate. A. Kurtenacker found that the reduction of dichromate by nitrous acid, in the presence of potassium hydrosulphate, can be represented by $dx/dt=(K_1+K_2S^2)[H_2Cr_2O_7][HNO_2]$—*vide supra.* In all probability it is the undissociated nitrous acid, and not the nitrite ion, which takes part in the change. Similar, the catalytically accelerating action of the added acid, $KHSO_4$, $CH_3.CO_2H$, is probably to be attributed to the undissociated mols. (or HSO'_4 ions), and not the hydrogen ions. E. Frémy reduced osmic acid with nitrous acid; and N. W. Fischer, soln. of auric chloride and mercurous nitrate.

As an *oxidizing agent,* W. Zorn, P. Zechlin, J. D. van der Plaats, S. M. Tanatar, E. Divers, E. J. Maumené, P. de Wilde, etc., showed that it reacts with nascent hydrogen, forming nitric oxide, nitrous oxide, and nitrogen, as well as hydroxylamine and ammonia. B. Suler studied the electrolytic reduction of nitrites. Nitrous acid oxidizes hydriodic acid or potassium iodide liberating iodine: $2HI+2HNO_2=2H_2O+2NO+I_2$—this reaction was studied by C. Aeby, A. Bömer, R. Böttger, C. Ekin, F. Fischer, E. Frémy, C. R. Fresenius, H. Hager, H. Kämmerer, J. König, A. R. Leeds, F. Musset, P. C. Plugge, C. F. Schönbein, and A. D. Tschirikoff. According to M. Lombard, if the reaction with iodides occurs in the presence of oxygen, the nitrous acid is regenerated as fast as it disappears. Nitrous acid precipitates sulphur from hydrogen sulphide. C. A. Winkler, E. Frémy, A. Claus, E. Divers and T. Haga, A. Lidoff, F. Raschig, and R. Weber found that sulphurous acid is oxidized to sulphuric acid; F. Raschig, nitrous oxide, to nitric oxide; and F. Hefti and W. Schilt, hydrogen sulphide, to thiosulphate, sulphur—and ammonia. N. R. Dhar studied the induced reaction involving the effect of nitrites on the reduction of mercuric chloride by oxalic acid.

N. W. Fischer, L. Ernst, and A. Piccini and F. M. Zuco found that manganous and ferrous salts form nitric oxide and hydrogen: $2FeSO_4+H_2SO_4+2HNO_2=2H_2O+2NO+Fe_2(SO_4)_3$; O. Baudisch and P. Mayer found that nitrites are reduced quantitatively by an excess of ferrous hydroxide in neutral and alkalinc soln.; and on boiling soln. made alkaline with carbonates, the chief products are ammonia and nitrous oxide; in boiling alkali-lye, the nitrite is reduced quantitatively to ammonia. Alkali nitrates are also reduced quantitatively to ammonia by ferrous hydroxide in neutral soln., and in alkaline soln. containing 28 per cent. of sodium hydroxide. P. Falciola said that if a litre of water containing 0·0001 per cent. of sodium nitrite is treated with about 2 c.c. of sulphuric acid and then with excess of thiocyanate and about 0·1 grm. of ferrous sulphate, an orange coloration is readily developed; if only 0·00001 per cent. of the nitrite is present, the colour appears more slowly. O. von Dumreicher found that stannous chloride is oxidized by nitrous acid with the formation of nitrous oxide. I. M. Kolthoff observed that the oxidization of a nitrite to nitrate by potassium permanganate does not occur in alkaline soln. Good results are obtained by adding the nitrite soln. to a considerable excess of permanganate in presence of 4*N*-sulphuric acid, and after 15 minutes, titrating the excess with iodide and thiosulphate. I. Bellucci said that in the presence of fluorides, the permanganate yields its oxygen $Mn_2O_7\rightarrow Mn_2O_3+4O$; and in its absence, $Mn_2O_7\leftarrow 2MnO_2+3O$. A. Claus, and C. Ludwig and A. Kromayer showed that urea is oxidized; according to N. A. E. Millon; $CO(NH_2)_2+N_2O_3=CO_2+2N_2+2H_2O$; or, according to F. Wöhler and J. von Liebig, in the cold and in conc. soln., $2CO(NH_2)_2+N_2O_3=(NH_4)_2CO_3+2N_2+CO_2$. For the reduction of nitrous acid by stannous chloride to nitrous oxide, hyponitrous acid (*q.v.*), and hydroxylamine (*q.v.*), *vide infra,* constitution. M. Coblens and J. K. Bernstein found that nitric oxide, and no ammonia, is formed when a sodium nitrite soln. is added drop by drop to an acid soln. of titanous chloride; and hydroxylamine is formed with an acid soln. of stannous chloride. The reducing action of titanous chloride on nitrous acid does not get fully to work because of the escape of the gaseous intermediate products of the action—*vide supra,* nitrous oxide. O. Baudisch and P. Mayer found that nitrites are reduced quantitatively by excess of ferrous hydroxide in neutral and alkaline soln. In boiling soln. made alkaline with carbonates, nitrous oxide and ammonia are chiefly formed. In boiling alkali hydroxide soln., the nitrite is quantitatively reduced to ammonia. O. Baudisch said that the formation of nitrate from nitrite by complex iron salts is probably due to the unsaturated tervalent nitrogen atom of the nitrite attaching itself to the central iron nucleus by secondary valencies, and it is subsequently decomposed, forming nitric oxide. The reduction of alkali nitrite by potassium ferrocyanide and oxygen is said to occur by the displacement of a CN-radicle from the inner sphere of the complex by oxygen and a molecule of an alkali taking its place, the nitrite then decomposes, giving off nitric oxide which is displaced by oxygen. The decomposition of alkali nitrites by complex iron salts can be effected in daylight at ordinary temp. For the action with arsenious and sulphurous acids, *vide* the respective acids.

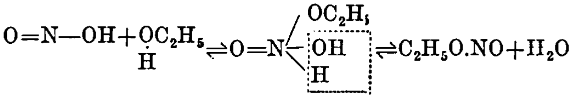
Nitrous acid is also employed as a *nitrating agent* in organic chemistry. Thus, M. F. Aitken and T. H. Reade studied its action on *p*-iododimethylaniline, and obtained nitro-derivatives; J. Reilly and P. J. Drumm, its action on substituted *p*-phenylenediamines; and F. Bettzieche, and R. H. A. Plimmer, its action on amides and other amino-compounds. Nitrogen trioxide was found by H. Reihlen and A. Hake to form an unstable complex with stannic chloride—possibly $3SnCl_4.4NO_2$. Nitrogen trioxide reacts with stannic chloride not in the ordinary blue but in the colourless form. A. Klemenc and R. Schöller studied the partition of nitrous acid between ether and water. The poisonous qualities of nitrous acid have been discussed by A. Purcell,[3] etc.

Some reactions of nitrous acid and the nitrites of analytical interest.—Many of the characteristic reactions of the nitrites depend on a change of colour attending oxidation or reduction. The salts are decomposed in the cold by sulphuric acid with the liberation of nitric oxide which gives brown fumes in air; the conc. acid acts more vigorously. Nitrates give brown fumes only when heated with the conc. acid. The test is not conclusive if chlorides or bromides be present. **Potassium iodide** is not decomposed by pure dil. nitric acid; whereas, a soln. of a nitrite, when acidified with dil. sulphuric or acetic acid, becomes yellow or brown owing to the separation of iodine. If a little starch paste be present, the soln. will be coloured blue. According to R. Böttger,[4] the reaction is sensitive to about one part of nitrous acid in about 10,000,000 parts of water. Many other oxidizing agents give the same coloration—ozone, hydrogen peroxide, chlorine, and ferric salts. Nitrates give the same coloration if a little zinc be added to the acidified soln. owing to the reduction of the nitrates to nitrites. A sensitive test for the nitrates is based upon the oxidation of **ferrous salts** by nitric acid: $6FeSO_4+3H_2SO_4+2HNO_3=3Fe_2(SO_4)_3+4H_2O+2NO$; and by nitrous acid; $2FeSO_4+H_2SO_4+2HNO_2=Fe_2(SO_4)_3+2H_2O+2NO$. In the cold, the nitric oxide forms a dark brown compound with the excess of ferrous salt. To apply the test, dissolve the nitrate in as little water as possible. Add a cold sat. soln. of ferrous sulphate slightly acidified with sulphuric acid. Pour conc. sulphuric acid down the side of the tube. If nitric acid be present, the zone of contact will be coloured dark brown. With nitrites, the conc. sulphuric acid need not be added. A warm, acidified soln. of **potassium permanganate** is decolorized by nitrous acid, but not a neutral soln. P. H. Hermans found that to 2 c.c. of the soln. to be examined a few drops of glacial acetic acid should be added and then 2 c.c. of 5 per cent. potassium oxalate soln., 1 c.c. of 5 per cent. **manganous sulphate** soln., and a few drops of 3 per cent. hydrogen peroxide. A red coloration indicates nitrite. A gram of sodium nitrite per litre can be detected in this way. If a nitrite be added to a dil., almost colourless soln. of **potassium ferrocyanide** acidified with acetic acid, G. C. Schäffer showed that a dark greenish-yellow colour appears—detectable if one part of nitrite is present in 600,000 parts of soln., owing to the conversion of ferro- to ferricyanide: $K_4FeCy_6+NaNO_2+2CH_3.COOH \rightarrow K_3FeCy_6+CH_3.COOK +CH_3COONa+H_2O+NO$. This reaction distinguishes nitrites from nitrates. The reaction was examined by C. M. van Deventer and co-workers, E. W. Davy, and T. M. Chatard. According to C. D. Braun, nitrites with potassium cyanide, cobalt chloride, and a little acetic acid give a reddish-orange colour. **Cobalt salts** with an excess of potassium nitrite and acetic acid give a yellow precipitate of potassium hexanitritocobaltate, $[Co(NO_2)_6]K_3$. According to E. Lenssen, W. Kalle and W. Prickharts, and P. Sabatier, **cuprous salts** in fuming hydrochloric acid soln. are coloured blue by nitrites. The colour vanishes when the soln. is warmed, or when alkalies are added. Nitrates may be distinguished from nitrites by the addition of hot concentrated sodium hyposulphite, the former remains unaltered, the latter evolves nitrogen. P. Falciola found that the addition of **sodium thiosulphate soln.** of about 0·5*N*-conc., drop by drop to an alkali nitrite soln. acidified with sulphuric acid, yields a transitory yellow coloration, more or less intense according to the proportion of nitrite present; this reaction is perceptible with 0·0001*N*-nitrite soln. With moderately conc. nitrite soln., use may be made of sodium thiosulphate test-paper, which is dipped first into the nitrite soln., and then into dil. sulphuric or acetic acid.

Several alkaloids are coloured by nitrites. In 1841, J. B. Berthemot found that **brucine** (0·02 grm.) in conc. sulphuric acid gives a red coloration with a soln. of nitrous acid mixed with 3–4 times its vol. of sulphuric acid. According to E. Nicholson, one part of nitric acid in 10,000,000 parts of water gives a perceptible pink coloration. The reaction was examined by G. Lunge, L. W. Winkler, and P. Pichard. Nitrous acid does not give the coloration in the presence of an excess of concentrated sulphuric acid. Aq. soln. of nitrites nearly always contain some nitrate, and consequently nitrites may appear to give the coloration. Nitrous acid in the presence of nitrates can be destroyed by treatment with dil. sulphuric acid and a concentrated solution of urea; or by boiling an alkaline soln. of ammonium nitrite with ammonium chloride—in both cases a trace of the nitrous acid is also converted into nitric acid. Chlorates react like the nitrates in the brucine test. A whole series of organic compounds give colour reactions with the nitrites or nitrates, and the intensity of the coloration is often proportional to the amount of, say, nitrite in a known vol. of soln., so that if the colour is matched in a colorimeter with a mixture containing a known amount of the nitrite, similarly treated, an estimate of the amount of nitrite in the given soln. can be made. For example, P. Griess showed that **m-phenylenediamine** gives a brown coloration with the nitrites—the equivalent of one part of nitrite in 10,000,000 parts of soln. gives a perceptible yellow colour. According to A. Longi, one part of nitric acid in 1,500,000 parts of water can be thus recognized. Other oxidizing agents like chloric acid, selenic acid, ferric chloride, chromic acid, vanadic acid, hypochlorites, hydrogen dioxide, etc., may give a similar coloration. The reaction was studied by E. M. Harvey.

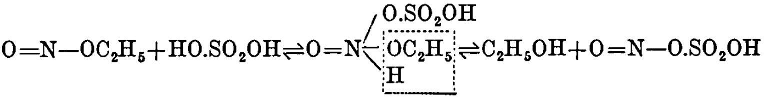
L. I. de Nagy Ilosva found that a mixed soln. of **sulphanilic acid and α-naphthylamine** gives a pink coloration when one part of nitrite is present in 1,000,000,000 parts of soln. E. Riegler observed that a mixture of **naphthionic acid** with a little conc. hydrochloric acid gives an intense rose coloration with nitrite soln. to which 20–30 drops of ammonia have been added—one gram in 10,000,000 c.c. can be so detected. H. Sprengel showed that when a few cubic centimetres of **phenol** dissolved in conc. sulphuric acid are poured over the dry mixture containing a nitrate, and after standing a moment, water is added, and the mixture is made alkaline with potassium (sodium, or ammonium) hydroxide, a yellow colour—due to the formation of tripotassium nitrophenol-disulphonate—develops if a nitrate be present. E. C. Woodruff found a dil. mixture of 2 drops of **dimethylaniline** and 0·2 grm. of *p*-toludine in 10 c.c. of sulphuric acid gives a blood-red colour with a nitrate in the presence of chlorates, bromates, or iodates; with chlorates it gives a strong brown colour. One drop of a 5 per cent. soln. of potassium nitrate in ten drops of the soln. of dimethylaniline gives an intense crimson in a few moments, and with one drop of a 0·001 per cent. soln. under similar conditions, a pale yellow. A. Tingle has shown that the following test for nitrates is not affected by the presence of halides. When a soln. of the nitrate is warmed with a 7 per cent. sulphuric acid soln. of **salicylic acid,** nitrosalicylic acid is formed, and when the soln. is made alkaline, a yellow or orange colour is produced. A. Jorissen, and A. Vogel found that **fuchsine** is coloured violet, blue, green, and finally yellow by nitrous acid; J. von Liebig, C. F. Schönbein, H. Trommsdorff, and H. Struve noted that **indigo** soln. is decolorized by nitrous acid; C. F. Schönbein, and M. Rosenfeld, **pyrogallol** is coloured brown; **resorcin,** by A. Novelli, E. Barbet and E. Jandrier, and G. Denigès; and P. Griess, **diamidobenzoic acid** is coloured yellow, orange-red, or brown. Colour reactions with 1 : **3-toluylene-diamine,** by P. Griess; **indol,** by O. Bujwid, and L. Spiegel; **phenol,** by C. P. Plugge; **diphenylamine,** by E. Kopp, and P. Soltzien; **aniline sulphate,** by T. M. Chatard, and G. Denigès; **aniline phosphate,** by P. Falciola; **p-amidobenzolazodimethylaniline,** by R. Meldola; **diphenyl-o-toluidine,** by C. Haussermann and R. Bauer; ammoniacal soln. of **cochineal,** by C. F. Schönbein; **antipyrine,** by M. C. Schuyten; **guaiacol,** by L. Spiegel; etc.

The constitution of nitrous acid and the nitrites.—The formula HNO_2 has been confirmed by analyses of the salts; by the electrical conductivity of the sodium salt; and by the effect of the acid on the f.p. of water. J. W. Brühl [5] considered that the refraction and dispersion of the aq. soln. corresponded with the presence of the hydrate $HNO_2.H_2O$, or of *orthonitrous acid,* $N(OH)_3$; the ordinary acid is then *metanitrous acid,* and the ordinary salts *metanitrites.* Salts are known corresponding with a theoretical pyronitrous acid, $N_2O(OH)_4$, obtained by the condensation of two mols of orthonitrous acid accompanied by the loss of a mol of water. There is some difference of opinion which of the formulæ $O_2{\equiv}N{-}H$; $O_2N{-}H$; or $O{=}N{-}OH$ represents nitrous acid. The last formula is generally accepted on the assumption that (i) the acid probably contains a hydroxyl group; and (ii) the nitrogen atom is tervalent. The first two formulæ are representative of formulæ in which the hydrogen atom is directly united to the nitrogen atom; and in the other type of formula, an oxygen atom intervenes; the former was suggested by R. Günsberg to explain the fact that silver nitrite, when gradually heated, forms nitric oxide with the simultaneous formation of metallic silver and silver nitrate; while if it be strongly heated, nitric peroxide and the metal are alone formed; hence, he argued that silver nitrite has the formula $Ag{-}NO_2$ where the silver atom is directly united to the metal. It is supposed that when silver nitrite is decomposed at a high temperature: $AgNO_2 \rightarrow Ag+NO_2$, and that at the low temp., the secondary reactions $Ag+2NO_2 \rightarrow AgNO_3+NO$, and also $AgNO_2+NO_2 \rightarrow AgNO_3+NO$, occur. The test on silver nitrite with phosphorus oxychloride for hydroxyl groups fails because no nitrogen oxychloride can be detected among the products of the reaction, and, even if such were formed, it is probable, as A. Exner has observed, that it would be decomposed by silver nitrite. A. von Bäyer and V. Villiger suppose that nitrous acid can unite with water or alcohol, forming addition compounds of the type:



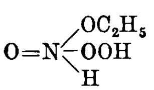
$$O{=}N{-}OH+\underset{H}{OC_2H_5}\rightleftharpoons O{=}N\begin{matrix}\diagup OC_2H_5\\ -\boxed{\begin{matrix}OH\\ H\end{matrix}}\\ \diagdown\end{matrix}\rightleftharpoons C_2H_5O.NO+H_2O$$

The unstable addition compound readily breaks down into ethyl nitrite and water: similarly, during the saponification of ethyl nitrite by dil. sulphuric acid, $HO.SO_2OH$, A. von Bäyer and V. Villiger suppose that

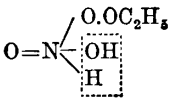


$$O{=}N{-}OC_2H_5+HO.SO_2OH\rightleftharpoons O{=}N\begin{matrix}\diagup O.SO_2OH\\ -\boxed{\begin{matrix}OC_2H_5\\ H\end{matrix}}\\ \diagdown\end{matrix}\rightleftharpoons C_2H_5OH+O{=}N{-}O.SO_2OH$$

and that the nitrosulphonic acid, $O{=}N{-}O.SO_2OH$, passes into the tautomeric form, $O{=}NO{-}O.SO_2OH$. The fact that ethyl nitrite reacts with hydrogen dioxide, forming nitric acid and alcohol, while nitrous acid and ethyl peroxide, $C_2H_5O.OH$, give ethyl nitrate and water shows that the addition products in the two cases are not the same; the hydrogen dioxide does not break into the two hydroxyl groups, but behaves like sulphuric acid, $H.O,SO_2OH$ as if it were $H.O.OH$, and similarly with ethyl peroxide, so that the addition compounds are respectively:

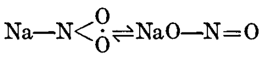


$$O=N\begin{smallmatrix}OC_2H_5\\OOH\\H\end{smallmatrix}$$



$$O=N\begin{smallmatrix}O.OC_2H_5\\OH\\H\end{smallmatrix}$$

This hypothesis explains very well the curious behaviour of the nitrites on the assumption that the molecule is O=N—OH. V. Meyer's experiments showed that when ethyl iodide, C_2H_5I, acts upon silver nitrite, both *ethyl nitrite*, $C_2H_5O.NO$, boiling at 18°, and *nitroethane*, $C_2H_5NO_2$, boiling at 114°, are formed. The fact that the reduction of ethyl nitrite with hydrogen sulphide, or with zinc and hydrochloric acid, produces ethyl alcohol, C_2H_5OH, and ammonia, is taken to mean that the ethyl group, C_2H_5, is not directly united to the nitrogen atom; otherwise, said A. Geuther, the ethyl radicle would stick to the nitrogen atom, and the reduction would give ethylamine, $C_2H_5NH_2$. On the other hand, it can also be argued that because methyl iodide, CH_3I, yields only nitromethane, CH_3NO_2, while the higher alkyl iodides give larger and larger propositions of alkyl nitrites, and are additively associated with the nitrous acid, forming alkyl nitrites, the formula for the nitrites is probably $H—NO_2$. The formation of the alkyl nitrites in these reactions may be considered as a secondary effect. The nitroparaffins are less stable than the alkyl nitrites when heated; and more stable in the presence of water. The fact that while silver nitrite in soln. forms metallic silver and nitric acid, silver nitrate is quite unaffected, is taken by E. Divers to mean that while hydrogen can separate silver from oxygen, it cannot separate it from nitrogen, and that in the nitrites silver must accordingly be directly united with hydrogen, $H.N : O_2$, and in the nitrates with oxygen, $HO.NO_2$. V. von Richter favoured the same hypothesis. P. C. Ray and P. Neogi have also shown that nitrites of potassium, sodium, barium, or calcium with ethyl alcohol and sulphuric acid give ethyl nitrite, $C_2H_5O.NO$, and nitroethane, $C_2H_5.NO_2$. With the alkali salts traces of *nitrobutane*, $C_4H_9.NO_2$, are also formed. This is taken to mean that the **metal nitrites have both a nitronic or imidic structure, M.N : O_2, and a hydroxylic structure, MO.N : O, that is, the salts are desmotropic.** F. Raschig found that when nitrous acid, or rather sodium nitrite, is reduced by stannous chloride, about 90 per cent. furnishes nitrous oxide, and 10 per cent. hyponitrous acid and hydroxylamine; the nitrite soln. contains



$$Na—N\Big\langle\begin{smallmatrix}O\\O\end{smallmatrix}\rightleftharpoons NaO—N=O$$

about 10 per cent. of the former, and 90 per cent. of the latter. H. Burgarth, H. Remy, and H. Henstock discussed the electronic structure.

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§ 38. The Nitrites

The occurrence of **ammonium nitrite**, NH_4NO_2; and its formation during the combustion of many substances in air; during the evaporation of water; by the oxidation of ammonia in air in the presence of a catalytic agent; by electrical discharges in moist air; by oxidizing ammonia with hydrogen dioxide or potassium permanganate; and during the decay of organic substances in air, have been previously discussed. J. J. Berzelius[1] prepared ammonium nitrite by treating lead nitrite with ammonium sulphate, or silver nitrite with ammonium chloride. M. Berthelot used barium nitrite and ammonium sulphate; and he also obtained it from ammonia, nitric oxide, and oxygen. P. Neogi and B. B. Adhicary obtained ammonium nitrite in fairly large quantities by evaporating and subliming in vacuo a very conc. soln. of a mixture of ammonium chloride and sodium or potassium nitrite. N. A. E. Millon obtained ammonium nitrite, mixed with the nitrate, by passing the gases obtained in the thermal decomposition of lead nitrate into aq. ammonia. The filtrate in all these cases can be evaporated in vacuo over quicklime. O. L. Erdmann, and S. P. L. Sörensen have discussed the preparation of this salt.

In their process, the mixture of nitrogen oxides evolved during the action of arsenic trioxide on nitric acid is passed over coarsely powdered ammonium carbonate kept cool by ice. The half liquid mass is treated with alcohol, the unchanged carbonate filtered off, and the ammonium nitrite precipitated by the addition of ether. The nitrite so obtained is of 90–94 per cent. purity, and may be purified by re-solution in 96 per cent. alcohol and reprecipitation with ether.

Ammonium nitrite furnishes white, needle-like crystals which are very deliquescent. M. Berthelot said that the aq. soln. has a neutral reaction; and he gave for the heat of formation, $(2N,4H,2O)=64{\cdot}8$ Cals.; and J. Thomsen, $(N_2,2H_2O) = -71{\cdot}77$ Cals. P. C. Ray and co-workers found that ammonium nitrite gradually changes into nitrate; even during the process of crystallizing the aq. soln., traces of the nitrate are formed, and this the more the higher the temp. According to M. Berthelot, the solid salt decomposes very slowly in winter, and rapidly in summer: $NH_4NO_2=N_2+2H_2O$, and it cannot therefore be preserved in a sealed glass tube; S. P. L. Sörensen said that the purified dry salt can be safely kept in an atm. of hydrogen, and in the presence of ammonium carbonate and calcium oxide. It is best kept and transported under dry ether, free from alcohol. M. Berthelot observed that when the solid is heated on a water-bath, it appears quiescent for a few moments, and then detonates violently; it also detonates by percussion. If gradually heated on platinum foil, it volatilizes very quickly; and if placed on a hot foil, it burns with a pale flame. Although when heated in the ordinary way, the salt decomposes into nitrogen and water, there is a side reaction, for, as noted by Lord Rayleigh and W. Ramsay, some ammonia is formed, presumably: $3NH_4NO_2=NH_4NO_3+2NO+2NH_3+H_2O$; and the nitrate yields nitrous oxide as indicated by J. J. Berzelius. P. C. Ray and co-workers noticed that when heated under reduced press., the salt begins to sublime at about 32°–33°, and the temp. can be safely raised to 60° without the substance undergoing decomposition. The sublimate appears as a transparent, compact mass of crystals. They found that the sublimed salt is quite colourless, and absolutely devoid of the green tint. It is less hygroscopic, and far less liable to decomposition than the ordinary salt. When kept open in a desiccator the sublimed substance does not change, even after the lapse of five or six days, but slowly diminishes in weight from day to day. When kept, however, in a vacuum sealed tube, the salt can be preserved for any length of time. The crystals in the vacuum tube can be made to pass from one part to another by the application of gentle heat. The pure salt can be resublimed in a vacuum without any decomposition or residue of ammonium nitrate, provided the temp. of the bulb does not exceed 60°. Ammonium nitrate under similar conditions does not vaporize or decompose. This difference in property has been utilized in completely separating ammonium nitrite from the nitrate, with which it is often more or less admixed. Although there is a little decomposition, the vap. density can be determined, and it yields 32·0–35·0 when the theoretical value is 32·0.

M. Berthelot reported that the conc. aq. soln. decomposes more rapidly than the solid, and when shaken froths like champagne; and J. J. Berzelius said that the dil. aq. soln. decomposes at 50° into nitrogen and water so that the liquid retains its neutrality. The salt is readily soluble in water, and, added S. P. L. Sörensen, with the development of heat; it is readily but slowly dissolved by alcohol, and is precipitated from this soln. by ether, chloroform, or ethyl acetate. The conc. aq. soln. decomposes explosively like the solid when heated to 60°–70°, and with an acidified soln., the decomposition sometimes occurs at ordinary temp. N. A. E. Millon found that the decomposition is slow or fast according as the soln. is alkaline or acid. A single drop of ammonia added to the neutral soln. is sufficient to render the decomposition gradual, while a single drop of hydrochloric, nitric, or sulphuric acid causes it to take place suddenly. K. Arndt said that soln. of ammonium nitrite, prepared from silver nitrite and ammonium chloride, become alkaline after a certain time owing to the formation of ammonia; but V. H. Veley denied this. K. Arndt found that the addition of ammonia retards the decomposition, and V. H. Veley, that the decomposition is retarded or stopped by oxides, like calcium oxide, which liberate ammonia in the soln. It is also retarded by aliphatic or aromatic amines, by hydrazines, and to a less degree by amines. The decomposition is accelerated temporarily by the aliphatic amides, but not by other amides; it is also accelerated by benzoic sulphimide. E. Bohlig showed that very dil. soln. may be evaporated on the water-bath without decomposition; and A. Schöyen added that a soln. with one hundred-thousandth part of salt can be half distilled without the salt decomposing; a soln. with one five-hundredth part of salt when half distilled has 8·6 per cent. in the distillate and 82 per cent. in the retort, and 9·4 per cent. has decomposed. O. Löw found that the presence of platinum-black causes the dil. aq. soln. to decompose at ordinary temp.—a trace of nitric oxide is formed in the early stages of the decomposition. F. E. Brown measured the equilibrium press. V. H. Veley said that the addition of finely-powdered barium sulphate temporarily favours the evolution of gas. A. Angeli and G. Boeris said that the addition of salts with a common ion—say, sodium nitrite or ammonium chloride—accelerates the evolution of nitrogen, and hence inferred that the stability of very dil. soln. on the assumption that the salt is all ionized; but R. Wegscheider said that the inference might also be made that the reaction takes place between the two ions: $NH^{\cdot}_4+NO'_2=2H_2O+N_2$. A. A. Blanchard working with this hypothesis found that the only agents which accelerate decomposition are hydrogen ions and free nitrous acid. The presence of the acid involves a secondary reaction, in which nitric oxide is liberated, but the primary decomposition of nitrite is found to be independent of this. The gas evolved in the decomposition of the nitrite contains no nitrous oxide. The rate of decomposition is proportional to the concentration of $NH^{\cdot}_4$ and NO'_3, but it is probable that two independent processes go on simultaneously, each resulting in the liberation of nitrogen. V. H. Veley found that the start of the decomposition is very slow, owing, presumably, to the retention in the soln. of nitrogen gas; the reaction then rapidly increases to a maximum and afterwards decreases in accord with the unimolecular law $\log \{a/(a-x)\}=kt$, whether the reaction follows its normal course, or is accelerated by the addition of another substance. W. Biltz and W. Gahl showed that the reaction, apparently unimolecular in the presence of other salts, may be bimolecular with a soln. of ammonium nitrite alone; and they add that the change takes place between ammonium nitrite and the nitrous acid produced by the hydrolysis of the salt. P. C. Ray and S. C. Mukherjee observed that with dilutions 18·0 and 20·0 litres the degree of ionization of the salt is 0·91 and 0·81 respectively; and P. C. Ray and N. R. Dhar found the eq. conductivities of the soln. at dilutions $v=20{\cdot}7$, 62·1, 186·3, and 558·9 litres, are respectively 96·72, 104·54, 107·69, and 110·92, and the value at infinite dilutions is 126·3 at 20°. T. J. Pelouze examined the action of sulphuric acid on ammonium nitrite. N. R. Dhar showed that copper, zinc, etc., dissolve copiously in a soln. of ammonium nitrite, or in a soln. of a soluble nitrite and an ammonium salt, and that the result is not due as K. A. Hofmann and G. Buhk supposed to the hydrolysis of the nitrite and the formation of free nitrous acid, because the metal is attacked even in the presence of urea which destroys the nitrous acid, and soln. of nitrite which are hydrolyzed—*e.g.* zinc, nitrite —do not attack copper. The action is attributed to the instability of ammonium nitrite and its ready decomposition into nitrous oxide and water. D. Berthelot and H. Gaudechon said that a soln. of ammonium nitrite is decomposed when exposed to ultra-violet light, and that nitrogen is in consequence evolved. M. Holmes was unable to confirm this. The very slight difference in the results with soln. exposed to ultra-violet light and kept in darkness for 9 hrs. is fully explained as purely thermal effects. P. C. Ray and J. N. Rakshit described a number of alkylammonium nitrites.

According to C. Paal, **hydroxylamine nitrite** is formed in aq. soln. when a 2 per cent. aq. soln. of hydroxylamine chloride is treated with silver nitrite at 0°. No evolution of gas occurs. It will be observed that hydroxylamine nitrite, $NH_3OH(NO_2)$, and ammonium nitrate, NH_4NO_3, are isomeric. A. P. Sabanéeff and co-workers observed a number of analogous cases. When hydrazine is treated with nitrous acid, T. Curtius showed that the nitrite primarily formed decomposes: $N_2H_4+HNO_2=N_3H+2H_2O$—*vide* hydrazoic acid. According to A. W. Browne and O. R. Overman, potassium nitrite oxidizes hydrazine sulphate in sulphuric acid with the formation, under comparable conditions, of larger yields of azoimide and of much smaller yields of ammonia than are obtained by the action of hydrogen peroxide on hydrazine sulphate. B. B. Dey and H. K. Sen found that soln. of the metal nitrites react vigorously with hydrazine sulphate, even at 0°, evolving 2 vols. of nitrous oxide and one vol. of nitrogen; this agrees neither with the assumed existence of hydrazine mononitrite nor dinitrite. F. Sommer pointed out that the failure of B. B. Dey and H. K. Sen to prepare hydrazine nitrite from barium nitrite and hydrazine sulphate is due to the normal sulphate usually containing some disulphate as impurity, and it then behaves as an acid salt. Normal **hydrazine nitrite,** $N_2H_5NO_2$, was obtained by mixing solutions of barium nitrite and neutral hydrazine sulphate, stirring to convert the thick, gelatinous barium sulphate into the crystalline form, and filtering by means of a vacuum. The stable solution is then evaporated in a vacuum over phosphoric oxide. The oil thus obtained does not crystallize spontaneously, but does so on inoculating with a small quantity of solid obtained by extracting a portion with methyl alcohol, partly precipitating with ether, and cooling in ether and solid carbon dioxide. The solid salt is almost white, but becomes yellow on fusion. It is hygroscopic, and dissolves readily in alcohol, but not in ether, and may be obtained from a mixture of these in large, probably monoclinic, prisms. It explodes violently with a blow, less vigorously if rapidly heated. Hydrazine nitrite decomposes according to the equation $N_2H_5NO_2=NH_3+N_2O+H_2O$, and this decomposition is very greatly accelerated by nitrous acid. The preparation of **hydrazine dinitrite,** $N_2H_6(NO_2)_2$, in aq. soln., is thus impossible, as the weakly basic character of hydrazine would cause the salt to be so far hydrolyzed that much nitrous acid would be present in the solution. If hydrazine disulphate and barium nitrite react together, the products are ammonium nitrite and nitrous oxide. The decomposition of hydrazine nitrite is thus due to the action of nitrous acid on the undissociated compound, and is autocatalytic. The secondary reaction, the formation of hydrazoic acid from hydrazine and nitrous acid, is due to the action of nitrous acid on the N_2H_5 ion.

Methods for the preparation of the alkali nitrites have been indicated in connection with nitrous acid. J. J. Berzelius,[2] E. Mitscherlich, N. W. Fischer, and J. Lang described the preparation of **potassium nitrite,** KNO_2, or of **sodium nitrite,** $NaNO_2$, by keeping the nitrates in a state of fusion for some time alone, or mixed with lead (W. Hampe, S. Feldhaus, and A. Stromeyer). The process was discussed by A. Lottermoser, and E. W. Albrecht. According to J. Milbauer, the reduction of sodium nitrate to nitrite is best effected by heating the salt with an excess of 15 per cent. of granulated lead. The reaction commences at the m.p. of the nitrate, and, after 2 hrs. at 420°, complete reduction is obtained, but less lead than the theoretical amount is oxidized owing to a certain proportion of the salt being decomposed thermally with the evolution of oxygen. Other reducing agents can be employed—*e.g.* iron (O. L. Erdmann, and Balzer and Co.) ; copper (J. Persoz) ; ferrous oxide (Chemische Fabrik Grünau) ; manganous, chromic, or arsenious oxide in the presence of free alkalies or alkaline earths (C. Huggenberg) ; sulphur (L. G. Paul) ; sulphur or pyrites (Chemische Fabrik Leopoldshall) ; calcium sulphide (J. Grossmann) ; barium sulphide (G. A. le Roy, and Y. Okae) ; zinc blende (L. Elsbach and B. Pollini) ; galena (H. N. Warren, and M. Bartsch and M. Harmsen) ; anhydrous sulphites (Chemische Fabrik Gränau, and A. Étard) ; carbon (A. Knop) ; calcium carbide (E. Jacobsen) ; starch (R. Warington). G. Tacchini compared the results by using manganese dioxide, ferric oxide, barium oxide, cobalt oxide, nickel oxide, cerium dioxide, and thorium dioxide, and obtained the best results by heating the sodium nitrate with 25 per cent. of barium oxide or manganese dioxide at 650°. Molten alkali nitrate was also reduced to nitrite by exposure to carbon monoxide (M. Goldschmidt) ; or producer gas (G. de Bechi and A. Thibault) or hydrogen (E. T. Chapman). A. Müller reduced an aq. soln. of sodium nitrate by electrolysis with an amalgamated copper cathode ; C. Stahlschmidt reduced an aq. soln. of potassium nitrate with zinc. J. L. Gay Lussac, and J. Fritzsche passed nitrogen trioxide or peroxide gases into alkali-lye. E. Divers recommended this process, and said that it is a mistake to suppose that the soln. contains much nitrate. It can be made with so little nitrate that the impurity can scarcely be detected.

Avoiding, so far as practicable, the use of cork and caoutchouc, nitrous gases, from nitric acid and starch or arsenious oxide, are passed into the concentrated soln. of the hydroxide or carbonate until the alkali is quite neutralized. Sodium carbonate alone is somewhat inconvenient, because of its sparing solubility, but this may be circumvented by adding it, finely divided and in sufficient quantity, to its own saturated soln., just before passing the gases and by often shaking the vessel during their absorption. To prevent free access of air, the nitrite is prepared in a flask with its mouth kept loosely closed while the gases are passing ; it is not necessary to cool the flask. The strength of the nitric acid and the temperature of the generator of the nitrous gases must be regulated that just a little nitric oxide is in excess of the nitric peroxide, and therefore is passing unabsorbed, as a guarantee that the latter does not act on the soln. in absence of its equivalent of the former and thus produce some nitrate. To free the gases from volatilized nitric acid, they may be passed through a bottle or tube, either empty or packed loosely with cotton.

The finished soln. must be almost neutral, and if acid must be boiled until neutral, before exposing it to the air. A conc. soln. of alkali nitrite dissolves a little nitrous acid without decomposing it, as water alone would. To obtain the salt in the solid state or to crystallize out the sodium nitrite where it is necessary to be sure of absence of all nitrate in it, the soln. may be freely evaporated, even at boiling heat, without decomposing or oxidizing it.

The production of the nitrites by the arc process of nitrogen fixation has been previously discussed. H. K. Benson made sodium nitrite from the gases obtained in the arc process of nitrogen fixation ; and the Nitrum Aktien-Gesellchaft, from the gases obtained in the oxidation of ammonia. G. A. le Roy prepared alkali nitrite by the action of nitric oxide on barium dioxide followed by treatment with an alkali salt. H. N. Warren obtained the nitrite synthetically by passing a mixture of ammonia and oxygen over platinized asbestos and then into alkali-lye. J. J. Berzelius, and J. Lang treated barium or lead nitrite with potassium carbonate, or silver nitrite with potassium chloride ; H. Schwarz saponified amyl nitrite with alcoholic potash. J. Lang obtained **lithium nitrite,** $LiNO_2$, by the action of lithium chloride on silver nitrite ; and F. Vogel, and W. C. Ball and H. H. Abram, by the action of lithium sulphate on barium nitrite.

The sodium salt was analyzed by C. H. Hess, J. Lang, W. Hampe, M. Oswald, and E. Divers, and it is anhydrous ; but J. Lang, and W. Hampe found the magma of crystals of potassium nitrite dried in vacuo to be **hemihydrated potassium nitrite,** $KNO_2.\frac{1}{2}H_2O$. E. Divers, M. Oswald, and P. C. Ray, however, found the air-dried salt to lose about one per cent. in weight by fusion, and hence inferred that this salt, too, is anhydrous. J. Lang, and F. Vogel say that **hemihydrated lithium nitrite**, $LiNO_2.\frac{1}{2}H_2O$, is formed when the salt is dried in a current of dry hydrogen. M. Oswald obtained this salt and also **monohydrated lithium nitrite,** $LiNO_2.H_2O$; the transition temp. is 49°, and the conditions of equilibrium are illustrated by Fig. 77. P. C. Ray, and W. C. Ball and H. H. Abram found that it crystallizes as the *monohydrate*, $LiNO_2.H_2O$, in white, flat, needle-shaped crystals from its aq. soln. All the alkali nitrites can be dehydrated in vacuo, over phosphorus pentoxide, without undergoing decomposition.

All these alkali nitrites furnish crystalline masses. E. Divers said that sodium and potassium nitrites are a faint yellow colour, and give yellow soln. with water. W. C. Ball and H. H. Abram, and M. Oswald said that the lithium salt is white. The lithium and sodium salts are deliquescent, and the potassium salt is very much so. Potassium nitrite furnishes small, thick, prismatic crystals, and sodium nitrite often gives large flat prisms, which, according to A. Fock, belong to the rhombic system, and have the axial ratios $a : b : c = 0{\cdot}6399 : 1 : 0{\cdot}9670$. M. Oswald gave 1·912 at 0°/0° for the sp. gr. of potassium nitrite which has been fused ; 2·168 at 0°/0° for the sodium salt ; and 1·615 at 0°/0° for monohydrated lithium nitrite. The sp. gr. of a soln. of potassium nitrate with 10 per cent. of salt is 1·049 ; with 30 per cent., 1·208 ; with 50 per cent., 1·377 ; and with 70 per cent., 1·599. J. G. Bogusky said the change in the sp. gr. of a soln. with conc. can be represented by a straight line being at 19·23°/19·23°, for 2·63, 20·11, and 48·89 per cent. soln. respectively 1·0174, 1·1401, and 1·3451. A sat. soln. of the potassium salt has a sp. gr. 1·6464 at 17·5°, it contains 74·5 per cent. of salt, and its b.p. is 132° at 758·5 mm. ; that of the sodium salt has a sp. gr. 1·3585 at 20°, it contains 45·8 per cent. of salt, and its b.p. is 128° at 761·5 mm. ; and that of the lithium salt has a sp. gr. 1·3186 at 19°, and it contains 48·9 per cent. of anhydrous salt. P. Rehbinder found at 20°, the surface energy, σ ergs per sq. cm., and the sp. gr., D, at 20°/4°, for soln. with p per cent., of water :

p	24·6	34·2	50·0	70·0	80·0	100·0
D	1·635	1·530	1·361	1·192	1·111	0·9982
σ	95·0	88·0	81·7	77·4	76·0	72·75

P. W. Bridgman found that potassium nitrite exhibited a polymorphic transition at the following press., p kgrms. per sq. cm., and temp. ; and it also exhibited the change in vol., δv c.c. per gram; the effect of press. on the transition temp., $d\theta/dp$; the latent heat of the transformation, L kgrm.-metres per gram; and the change of energy, E, kgrm. m. per gram:

p	5000	6000	7000	8000	9000	9500	10,000
θ	−3·0°	14·0°	31·4°	50·8°	74·4°	89·4°	109·3°
δu	0·0312	0·0327	0·0341	0·0355	0·0369	0·0376	0·0383
$a\theta/dp$	0·0169	0·0171	0·0182	0·0212	0·2274	0·0343	0·0472
H	4·99	5·49	5·71	5·42	4·68	3·97	3·10
E	3·43	3·53	3·32	2·58	1·36	0·40	−0·73

E. Divers, and W. C. Gangloff found the m.p. of the sodium salt to be 271°; C. Matignon and G. Marchal, 276·9°; M. Oswald gave 217° for this salt; 297·5° for the potassium salt; and 97° for the hemihydrated lithium salt. According to P. C. Ray, when potassium nitrite is heated the first stage of the decomposition involves two concurrent reactions: $3KNO_2=K_2O+KNO_3+2NO$; and $4KNO_2=K_2O+2KNO_3+NO+N$. Afterwards, nitric oxide, oxygen, and nitrogen are evolved, part of the nitric oxide and oxygen being absorbed by the alkali oxide which is formed: $K_2O+2NO+O=2KNO_2$. As the temp. rises more oxygen is evolved, together with nitric oxide, and nitrogen peroxide. P. C. Ray suggested that as a result of the purely thermal decomposition, a portion of the salts breaks up into the peroxide and nitric oxide, but as the former is unstable, especially under diminished press. at the temp. at which the scission takes place, it parts with its oxygen both to the nitric oxide and also to the remaining portion of the undecomposed salt in a state of fusion, and that it is in this way that the internal oxidation and reduction are brought about. M. Oswald found that the temp. of decomposition at about 0·05 mm. press. is 185° for anhydrous lithium nitrite; 320° for sodium nitrite; and 350° for potassium nitrite. C. Matignon and G. Marchal gave $(N_{gas},O_{2gas},Na)=88{\cdot}2$ Cals.; and $HNO_{2soln.}+NaOH_{soln.}=NaNO_{2soln.}+H_2O+11{\cdot}1$ Cals.; $2NaNO_{2soln.}+H_2SO_{4soln.}=Na_2SO_{4soln.}+2HNO_{2soln.}+9{\cdot}2$ Cals.; and the heat of soln., $(NaNO_2,Aq.)=-3{\cdot}52$ Cals. C. Matignon and E. Monnet gave for the heat of oxidation $2NaNO_{2solid}+O_{2gas}=2NaNO_{3solid}+45$ Cals. According to M. Berthelot and J. Ogier, the heat of the reaction $(N_2O_{3aq.}K_2O_{aq.})=10{\cdot}6$ Cals. H. Helberg found that the mol. depression of the f.p. of sodium nitrite is normal, and does not show the irregularities recorded by M. Oswald. G. Tammann found the lowering of the vap. press. of water at 100° by the addition of 14·02, 110·03, and 229·01 grms. of potassium nitrite per 100 grms. of water to be respectively 36·9 mm., 241·1 mm., and 370·5 mm.; and with 3·02, 56·85, and 111·71 grms. of sodium nitrite per 100 grms. of water, respectively 10·1 mm.; 194·0 mm.; and 318·3 mm. J. G. Bogusky found the index of refraction, μ, of soln. of sodium nitrite at 20°, and the D-line, is $\mu=1{\cdot}33336+0{\cdot}0011559w$, where w denotes the per cent. $NaNO_2$ in soln. R. Robl observed no fluorescence with the salt in ultra-violet light. M. Schümann gave for the eq. conductivity, λ, of sodium nitrite, one mol in v litres, at 25°:

v	32	64	128	256	512	1024	∞
λ	102·0	104·4	107·2	109·6	110·8	113·0	115·5

so that $\lambda_{1024-32}=11{\cdot}0$. S. von Niementowsky and J. von Roszkowsky obtained higher values with probably a less purified sodium salt; for potassium nitrite, they gave:

v	32	64	128	256	512	1024	2048
λ	147·7	151·1	155·1	158·6	161·9	166·9	172·7

P. C. Ray and N. R. Dhar also measured the electrical conductivities of soln. of potassium and sodium nitrites, and they found for lithium nitrite, at 20°:

v	6	18	54	162	486	∞
λ	70·32	75·00	91·52	100·00	102·05	93·7

P. C. Ray and S. C. Mukherjee found the degrees of ionization of potassium nitrite of dilutions v=16·0 and 36·0 litres to be respectively 0·86 and 0·91 ; and for sodium nitrite for v=10·0 and 20·5 litres, respectively 0·87 and 0·91. F. H. Jeffrey found that the electrolysis of soln. of sodium nitrite with aluminium electrodes resulted in the formation of aluminium hydroxide, and nitric oxide, while nitric acid was found in the anolyte. The primary product at the anode is probably aluminium nitrite which is hydrolyzed to nitrous acid and aluminium hydroxide ; and the nitrous acid then forms nitric oxide and nitric acid.

J. Obermiller measured the hygroscopicity of potassium nitrite. E. Divers said that at 15°, potassium nitrite is soluble in about one-third its weight of water ; and 5 parts of sodium nitrite require 6 parts of water for dissolution ; and J. Lang added that lithium nitrite is easily soluble in water. W. C. Ball and H. H. Abram found that lithium nitrite melts below 100° in its water of crystallization ; it is dehydrated rapidly at 160° and at the same time loses traces of nitrogen oxides. It is very soluble in water, and a sat. soln. at ordinary temp. contains 90 grms. of the monohydrate per 100 c.c. of soln. It is only sparingly soluble in absolute alcohol, whereas the potassium salt is fairly soluble. M. Oswald's solubility curves are shown in Figs. 75–77. The ice-curve with potassium nitrite falls to the eutectic at —31·6° with 71·8 per cent. KNO_2 ; and the solubility represented by the amount of salt, S, dissolved by 100 parts of water, is :

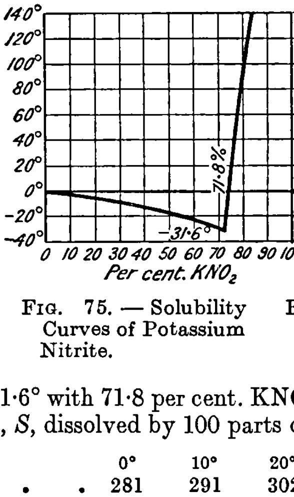


FIG. 75. — Solubility Curves of Potassium Nitrite.

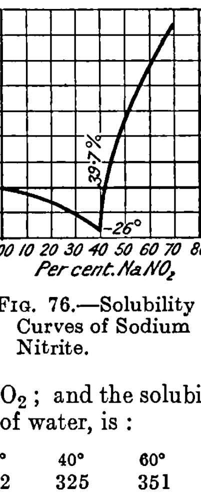


FIG. 76.—Solubility Curves of Sodium Nitrite.

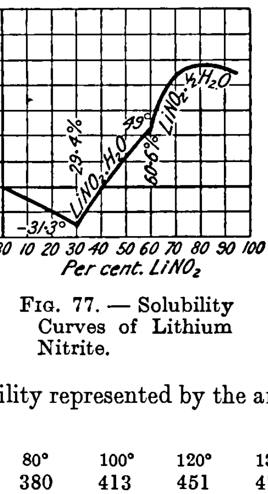


FIG. 77. — Solubility Curves of Lithium Nitrite.

	0°	10°	20°	40°	60°	80°	100°	120°	130°
S . .	281	291	302	325	351	380	413	451	473

and for θ° between —30° and 130°, $S=(600\theta+656600)/(2334-6\theta)$. The ice-curve with sodium nitrite has a eutectic at —15·5° with 39·7 per cent. of $NaNO_2$; but H. Helberg showed that the eutectic is at —26° with 38 per cent. of sodium nitrite ; and the solubility, S, is :

	0°	10°	20°	40°	60°	80°	100°	120°
S . .	73	78	84	98·5	116	136	160	198·5

The ice-curve with lithium nitrite has a eutectic at —31·3° with 29·4 per cent. of $LiNO_2$. There is a transition point at 49° and 60·6 per cent. $LiNO_2$ corresponding with the change : $LiNO_2.H_2O \rightleftharpoons \frac{1}{2}H_2O+LiNO_2.\frac{1}{2}H_2O$. The solubility, S, parts of the monohydrate in 100 parts of water, is :

	0°	10°	20°	30°	40°	50°
S	125	156	189	242	316	459

J. Lang, and W. Hampe said that in 90 per cent. alcohol, potassium nitrite forms an oily liquid ; it is insoluble in 94 per cent. alcohol ; and absolute alcohol precipitates the salt almost quantitatively from a conc. aq. soln. Sodium nitrite dissolves in warm 90 per cent. alcohol—it is scarcely soluble in 94 per cent. alcohol ; but absolute alcohol does not precipitate much salt from conc. aq. soln. C. A. L. de Bruyn found 0·31 grm. of sodium nitrite dissolves in 100 grms. of absolute ethyl alcohol at 19·5°. J. Lang said lithium nitrite is easily soluble in alcohol. E. C. Franklin and C. A. Kraus found sodium nitrite is soluble in liquid ammonia. J. Lang said the aq. soln. of potassium, sodium, and lithium nitrite are feebly alkaline; W. Hampe said neutral. H. Ley found the soln. of sodium nitrite, in water free from carbon dioxide, is alkaline to litmus, and neutral to phenolphthalein; C. Matignon and G. Marchal said that nitrous acid resembles nitric acid in its behaviour towards phenolphthalein, cochineal, litmus, *p*-nitrophenol, brazilin, and iodoeosin; but decomposes others—*e.g.* helianthin; and H. Friedenthal, and E. Salm found the neutral point of phenolphthalein corresponds with $10^{-9}N$-hydrogen ions; it follows that the conc. of the OH′-ions in the soln. will approximate $10^{-5}N$-soln. M. Oswald said that in conc. aq. soln., appreciable hydrolysis occurs at 100°: $3KNO_2+H_2O=2NO+2KOH+KNO_3$. J. Lang said that the aq. soln. of the alkali nitrites *nimmt langsam in Lösungen Sauerstoff auf*, but E. Divers has shown that these soln. can be safely evaporated on a water-bath, even at the boiling temp., without decomposition or oxidation; while P. C. Ray kept soln. evaporating spontaneously in flat dishes exposed to air between 25° and 30° for 2 months without the formation of an appreciable quantity of nitrate; and C. Russworm kept a soln. with 0·048 grm. KNO_2 per litre for a year without change. M. Oswald also detected no oxidation of the conc. soln. by oxygen at atm. press.; the aq. soln. are oxidized only in the presence of acids, and this is rather due to the oxidation of the decomposition products—nitric oxide—derived from nitrous acid itself. C. C. Palit and N. R. Dhar found that soln. of sodium nitrite are oxidized by air in the presence of ferrous hydroxide; W. P. Jorissen and C. van den Pol observed that sodium sulphite has no influence on the oxidation of soln. of sodium nitrite. W. Reinders and S. I. Vles found that pure sodium nitrite is not oxidized by oxygen in neutral or alkaline soln., but in the presence of a small quantity of nitric or other acid, it is converted into sodium nitrate. It is assumed that the formation of nitric oxide is an intermediate stage in the oxidation; the free nitrous acid is first oxidized to nitric oxide, nitrogen peroxide, and water; this is followed by the oxidation of nitric oxide to nitrogen peroxide; this reacts with water to form nitric oxide and nitric acid, which yields sodium nitrate and nitrous acid. Potassium nitrite behaves similarly. All strong acids produce the same effect, but the salts have no catalytic influence. The accelerating influence of iron and aluminium salts is due to their hydrolysis. N. R. Dhar also said that the oxidation of soln. of sodium nitrite by atm. oxygen can be induced by the simultaneous oxidation of sodium sulphite, stannous chloride, the hydroxides of manganese and cobalt, acetic acid, aldehyde, benzaldehyde, etc., by air. B. C. Banerji and N. R. Dhar found that the oxidation with iodine is sensitive to light. N. N. Mittra and N. R. Dhar observed that the oxidation of sodium sulphite by air is hastened by the simultaneous oxidation of sodium nitrite as a secondary reaction; but W. P. Jorissen and C. van den Pol found that sodium sulphite does not induce the oxidation of sodium nitrite by air or oxygen under ordinary conditions. C. Matignon and G. Marchal observed that an aq. soln. of sodium nitrite is not oxidized by prolonged contact with oxygen under a press. of 50–55 atm., even in the presence of a catalyst; but in an atm. of oxygen at 175 atm. and 395°–530° during 9 hrs., solid sodium nitrite is almost completely oxidized to nitrate—*vide supra*, nitrous acid. T. L. Bailey found that the loss of nitrite when sodium nitrite is dissolved in sulphuric acid of varying conc., and the soln. treated with a current of air, is a maximum with acid of sp. gr. 1·0–1·47. For the action of sulphurous and arsenious acids, *vide* the respective acids. H. Stamm measured the solubility of sodium nitrite in aq. ammonia. The dry nitrites are not attacked by nitric oxide, so long as the salt does not decompose. The salt is attacked by nitrogen peroxide: $NaNO_2+NO_2=NaNO_3+NO$; and $2NaNO_2+NO_2=2NaNO_3+N$. These reactions can take place when the nitrite is undergoing thermal decomposition when nitrogen peroxide is one of the products of the reaction. T. Curtius noted that ammonium chloride reacts with sodium nitrite, and when heated, nitrogen and sodium chloride are formed, presumably owing to the intermediate formation of ammonium nitrite. D. Tommasi said that if a crystal of ammonium chloride, sulphate, or nitrate be added to molten potassium nitrite, luminescence occurs. J. W. van Geuns found that a mixture of potassium nitrite and cyanide burns when ignited, but at 450° explodes violently. A. Angeli found that a mixture of sodium nitrite and thiocyanate detonates when heated—nitrohydroxylamine is stated to be an intermediate product of the reaction. According to W. Traube, sodium nitrite swells up considerably when exposed to the action of sulphur trioxide, forming a colourless, crystalline mass of **sodium nitroxyltrisulphonate,** $Na(SO_3)_3NO_2$, which is decomposed by water with the vigorous evolution of oxides of nitrogen. A. P. Lidoff observed that hyposulphurous acid reacts with a soln. of potassium nitrite, forming a hydroxylamine (*q.v.*). According to A. Gutmann, sodium thiosulphate does not act on a cold or boiling soln. of sodium nitrite; a mixture of the two is explosive. In a sealed tube at 100°, a mixture of sodium nitrite and calcium thiosulphate reacts: $2NaNO_2+2CaS_2O_3+4H_2O=2CaSO_3+Na_2SO_4+(NH_4)_2SO_4$. K. A. Hofmann and G. Buhk found that carbon monoxide is absorbed very slowly by a soln. of sodium nitrite. A soln. of sodium nitrite in the presence of an ammonium salt and copper gives off nitrous oxide. N. R. Dhar measured the solubility of ammonia and of carbon dioxide soln. of potassium nitrite. B. Suler studied the electro-reduction of potassium nitrite soln. whereby ammonia and hydroxylamine are formed.

R. H. Robinson found sodium nitrite to be unsuitable as a fertilizer, particularly in acid soils, owing to losses of nitrogen by decomposition. According to C. Marie and R. Marquis, nitrous acid is liberated from aq. soln. of the alkali nitrites by carbon dioxide, so that a strip of potassium iodide-starch paper suspended over the liquid is coloured blue. O. Baudisch found that the reduction of nitrite by potassium ferrocyanide and oxygen is sensitive to light. M. Oswald found that the presence of sodium sulphate lowers the solubility of sodium nitrite enormously—at 16°, a sat. soln. of the nitrite alone has 81·6 per cent. $NaNO_2$, but a sat. soln. of both salts together has 11·8 per cent. sodium sulphate, and 53·9 per cent. of sodium nitrite. The curves for the mutual solubility of sodium nitrite and nitrate at different temp. are shown in Fig. 78. The curve *AB* represents a soln. with two solid phases in equilibrium. There is no evidence of the formation of a double salt. E. B. Maxted found that when soln. of metallic sodium and sodium nitrite in liquid ammonia are mixed together yellow **disodium nitrite,** Na_2NO_2, is formed. The same substance is deposited on the cathode when a soln. of sodium nitrite in perfectly anhydrous liquid ammonia is subjected to electrolysis. The substance is decomposed vigorously by water with the formation of sodium nitrite, sodium hydroxide, and hydrogen. By passing a current of moist nitrogen over the disodium nitrite, the action is moderated, and the resulting soln. is found to be free from hydroxylamine and hyponitrite. According to W. Peters, when copper is warmed with a 5 per cent. aq. soln. of sodium nitrite at 60°, in the presence of carbon dioxide so as to exclude air, the gases contain nitrous and nitric oxides, and the soln. copper nitrate. The decomposition is chemical, not catalytic, and involves simultaneous oxidation and reduction. Lead, iron filings, and cobalt dissolve in the soln. without evolving gas, and, in the case of cobalt, sodium cobaltic nitrite is formed. F. E. Brown and J. E. Snyder observed no reaction with sodium nitrite and vanadium oxychloride. W. W. Lewis and co-workers discussed the use of sodium nitrite in the curing of meat.

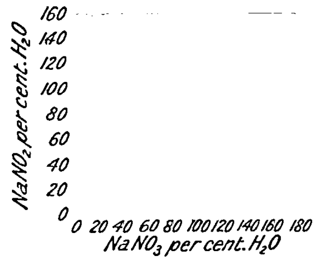
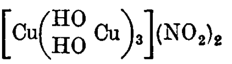


FIG. 78.—Solubility Curves of Mixed Solutions of Sodium Nitrite and Nitrate.

W. C. Ball and H. H. Abram prepared **rubidium nitrite,** $RbNO_2$, from soln.

of rubidium chloride and silver nitrate ; or preferably, barium nitrate and rubidium sulphate because the reaction with silver nitrite is complete only when all that salt is in soln., and it is a sparingly soluble salt. The evaporation of the soln. gives a pale yellow, deliquescent, crystalline mass. The salt retains only a little water at 100°. It is very soluble in water, and sparingly soluble in hot absolute alcohol. G. S. Jamieson prepared **cæsium nitrite,** $CsNO_2$, as a pale yellow, hygroscopic, indistinctly crystalline mass, from soln. of silver nitrite and cæsium chloride, or better, according to W. C. Ball and H. H. Abram, from barium nitrite and cæsium sulphate.

Normal **copper nitrite,** $Cu(NO_2)_2$, has not been definitely isolated in the solid state, but E. Péligot[3] claimed to have obtained it by keeping dihydrated cupric diamminonitrite for some days at 100°. J. J. Berzelius obtained a green liquid by the action of copper sulphate on lead nitrite. The soln. oxidizes in air, or when warmed, forming copper nitrate. When prepared in aq. media, H. Bassett and R. G. Durrant showed that cupric nitrate undergoes complex changes, and at ordinary temp., nitric oxide is evolved. E. Divers and T. Haga found that the dark green liquid, obtained by the action of copper on a soln. of silver nitrate or by mixing soln. of copper sulphate and potassium nitrate, contains some hydroxylamine. P. C. Ray obtained a dark green soln. by the action of nitric acid on copper in excess ; and also by the action of copper sulphate on barium nitrite, or of silver nitrite on copper chloride. L. I. de Nagy Ilosva obtained it by treating an ammoniacal soln. of copper nitrite with hydroxylamine chloride. W. Hampe said that the green soln. develops nitric oxide at ordinary temp., and P. C. Ray reported that a dil. soln. in air gradually forms the nitrate, and when conc. over sulphuric acid, under diminished press., forms nitric oxide by autoxidation. E. Divers considered that no autoxidation occurs, rather is the action produced by the oxygen of the air, and the hydrolysis of the nitrous acid. P. C. Ray and N. R. Dhar found that the aq. soln. is feebly acidic, and for dilutions with a mol of the salt in 18·12, 54·36, 162·58, and 487·74 litres, at 20°, the conductivities are respectively 58·55, 79·92, 99·46, and 111·18 ; when the calculated value at infinite dilution is 106·8 at 20°. N. W. Fischer said that when the attempt is made to conc. the soln. by evaporation, blue scales of a basic salt are formed ; W. Hampe said that if the soln. be evaporated in vacuo, and the residue washed with water, the product is **copper oxynitrite,** $CuO.Cu(NO_2)_2$, which, according to P. C. Ray, also contains a little nitrate. B. van der Meulen reported **copper hexahydroxydinitrite,** $3Cu(OH)_2.Cu(NO_2)_2$, which A. Werner represented as a hexol salt:



$$\left[Cu\left(\begin{matrix}HO\\HO\end{matrix}Cu\right)_3\right](NO_2)_2$$

by mixing eq. soln. of copper sulphate and potassium nitrite ; adding alcohol ; and evaporating the mixture at ordinary temp. The product is a mass of acicular crystals, which are stable at ordinary temp. ; readily soluble in dil. acids, and in aq. ammonia ; but sparingly soluble in water or alcohol. Boiling water decomposes the salt. H. Bassett and R. G. Durrant said that the compound does not explode by percussion. According to C. Przibylla, when a nitrite is added to a soln. of copper salt, the blue colour deepens, and a layer of conc. soln. one cm. thick is opaque. Presumably complex salts are formed. If an acid be added to the soln., nitrogen trioxide or nitric oxide is not immediately given off unless the soln. is warmed.

C. F. Schönbein said that if a soln. or mixture of cuprous or cupric oxide, or cupric carbonate in aq. ammonia, be exposed to air, some copper ammonionitrite is formed. E. Péligot reported **hydrated copper diamminohexanitrite,** $3Cu(NO_2)_2.2NH_3.H_2O$, to be formed in green crystals by the spontaneous evaporation of a soln. of **dihydrated copper diamminonitrite,** $Cu(NO_2)_2.2NH_3.2H_2O$. A soln. of this salt is said to be produced in violet needles by evaporating the soln. obtained by the action of aq. ammonia on copper while exposed to air, boiling the residue with alcohol sat. with ammonia, and cooling the filtered soln. The crystals are green at 100°, and slowly pass into cupric nitrite as indicated above. The salt explodes at a higher temp., or by percussion. It is soluble in water, with the absorption of heat, and the dil. soln. is hydrolyzed to cupric hydroxide, etc. There is a doubt about the individuality of E. Péligot's products—*vide infra*, the copper amminonitrites.

P. Pudschies obtained **copper tetramminonitrite,** $Cu(NO_2)_2.4NH_3$, by adding potassium nitrite to a soln. of copper diamminoacetate, and precipitating with alcohol and ether in the cold. H. Bassett and R. G. Durrant prepared copper tetramminonitrite by the action of air and aq. ammonia on copper filings (E. Péligot); by the extraction of the hexahydroxydinitrite with aq. ammonia; by the action of a conc. ammoniacal soln. of ammonium nitrite on cupric hydroxide; by the action of nitrous gases, from nitric acid and arsenic trioxide, on copper hydroxide suspended in aq. ammonia; and by evaporating at ordinary temp. the filtered soln. of the basic nitrite in the minimum amount of aq. ammonia, of sp. gr. 0·880. The salt forms dark blue, acicular crystals belonging to the tetragonal system. The conductivity of the aq. soln., and partition of ammonia between the salt and chloroform were measured by P. Pudschies. The electrical conductivities of a mol of the salt in 2·286 and 4·572 litres of water at 18° were respectively 68·4 and 73·0; and for a soln. in 9·144 litres, a precipitate of a basic salt was formed. H. Bassett and R. G. Durrant found that when the tetramminonitrite is exposed to moist air, while protected from dust, for about 3 months, a mixture of the diamminonitrite and the hexahydroxydinitrite is formed. Taking picric acid as 100, the sensitiveness of the tetramminodinitrite to shock is 89. The purified salt may be heated either slowly or rapidly without any explosion, but all specimens containing nitrate are apt to explode towards the end of the heating process. The explosion of the tetramminodinitrate is vigorous at 212°, and the loss of ammonia after two hrs.' heating at 200° in a continuous current of air was only 3 per cent., whereas the corresponding nitrite loses more than 15 per cent. at temp. below 100°, and this without any current of air. It appears, therefore, that ammonia is held firmly in the nitrate, but not in the nitrite, and that in mixtures the nitrite is quietly decomposed by heat, final explosion being due to subsequent action on the nitrate. H. Bassett and R. G. Durrant also prepared **copper diamminodinitrite,** $Cu(NH_3)_2(NO_2)_2$, as a purple powder by heating the finely divided tetramminodinitrite for 24 hrs. at 97°. The product readily dissolves in ammonia to form a perfectly clear blue soln., and on exposing the powder to an atm. containing dry ammonia at the ordinary temp., the violet-blue tetrammine nitrite was re-formed. If the sensitiveness of picric acid to explosion by shock is 100, that of the diamminodinitrite is 55. G. T. Morgan and F. H. Burstall prepared **copper bisethylenediaminonitrite,** $[Cuen_2](NO_2)_2$, by the action of silver nitrite on copper diaquobisethylenediamminoiodide. The dry salt is stable up to 120°; it melts with rapid decomposition at 128°. It is extremely soluble in water, but less soluble in alcohol. In aq. or alcoholic soln., the salt is not decomposed even on boiling; caustic alkalies have no effect, but dil. acid causes immediate evolution of nitrous fumes. Silver nitrate produces a quantitative separation of silver nitrite in alcoholic soln., showing that the dissolved complex nitrite is ionized in this medium. A. Fock prepared black needles of **potassium cupric nitrite,** $3KNO_2.Cu(NO_2)_2$, by evaporating in air a mixed soln. of an excess of potassium nitrite and cupric sulphate. The rhombic crystals appear green in thin layers, and have the axial ratios $a : b : c = 4992 : 1 : 0·8704$. They are stable in a desiccator, and decompose at 100°. The salt was also prepared by A. Kurtenacker.

J. L. Proust[4] first prepared **silver nitrite,** $AgNO_2$, by boiling an aq. soln. of silver nitrate with finely-divided silver for several hours; some metal was dissolved, and the evaporation and cooling of the pale yellow liquid furnished a yellow powder, which, after washing, was regarded as a sub-nitrate of silver. It was also precipitated from the yellow soln. by alcohol. H. Hess obtained the same salt by adding barium nitrite, prepared by the action of nitric oxide on baryta, to an aq. soln. of silver sulphate. He regarded it as a compound of nitric oxide with silver oxide.

The same salt was prepared by E. Péligot by adding barium nitrite to a soln. of silver nitrate. E. Mitscherlich, and V. Kohlschütter and E. Eydmann added sodium nitrite to a soln. of silver nitrate, and crystallized the precipitated silver nitrite (and oxide) from its soln. in boiling water; V. Meyer worked with potassium nitrite and silver nitrate; J. Persoz melted equal parts of silver and potassium nitrates, and crystallized the silver nitrite from hot water. E. Priwoznik treated an excess of silver with nitric acid; W. J. Russell, and A. R. Leeds passed hydrogen into a conc. soln. of silver nitrate; and E. Divers heated silver nitrate in a current of nitric oxide. The aq. soln. decomposes below 100°, and J. Lang, and N. W. Fischer said that the losses are so great when the attempt is made to purify the salt by recrystallization, that it is better instead to wash the salt with a little cold water. A. Naumann and A. Rücker crystallized the salt from a soln. of nitrous acid.

Analyses by A. Naumann and A. Rücker, J. Persoz, J. Lang, and E. Mitscherlich agree with the empirical formula $AgNO_2$. I. Kissel, J. Bewad, and P. C. Ray and P. Néogi found that when silver nitrite is treated with alkyl iodide, both ethyl nitrite and nitroethane are formed—*vide supra*, nitrous acid. It can therefore be inferred that the salt is tautomeric $Ag.ONO \rightleftharpoons Ag.NO_2$. The abnormally small ionization of silver nitrite in aq. soln. also led H. Ley and K. Schäfer to assume that only the form $Ag.O.NO$ is ionized in the normal way, while the form $Ag.NO_2$ is very little ionized. P. C. Ray and A. C. Ganguli reported that they have isolated these two forms. The one, **α-silver nitrite**, $Ag.NO_2$, is formed by double decomposition of silver nitrate and sodium nitrite in solution; the crystals which separate are washed with cold water and dried in vacuo over sulphuric acid. When the mother-liquid, left after the α-salt has separated, is allowed to stand a long time, crystals of the other salt, **β-silver nitrite**, $Ag.O.NO$, separate. The α-salt is said to decompose when melted between 220° and 250°: $2Ag.NO_2 \rightarrow 2Ag + N_2O_4$, with a side reaction: $Ag + N_2O_4 \rightarrow AgNO_3 + NO$; while the β-salt decomposes without melting, giving but little nitrogen oxide and much oxygen: $AgO.NO \rightarrow Ag + O + NO$. The scission of the β-molecule on the assumption that it is constituted $\mathrm{Ag}\rlap{\,\vdots}{-}\mathrm{O}\rlap{\,\vdots}{-}\mathrm{NO}$ is supposed to take place as indicated by the dotted lines; and of α-molecule $\mathrm{Ag}\rlap{\,\vdots}{-}\mathrm{NO}_2$. According to E. Divers, the alleged differences are not a question of a difference in constitution, but merely due to the difference in the state of subdivision of the two salts. He said: (i) Silver nitrite does not fuse but commences to decompose at 180°, and the observed fusion is due to the silver nitrate which melts below 217°. (ii) The observed difference in the two cases is due to some nitrate and residual nitric oxide in one case, and in the other case a little oxygen can be isolated. The difference in the way the salts pack in the tube and the consequent difference in the way the gases are temporarily imprisoned when the salt is heated sufficiently explain the observed results.

N. W. Fischer said that the powder is almost white, but the prismatic crystals are yellow, and this is the more pronounced the larger the crystals. Good crystals are obtained by the spontaneous evaporation of aq. soln. in darkness. J. Persoz obtained needle-like crystals which appeared colourless in the mother-liquor, but pale green when alone in air. A. Fock said that the crystals belong to the rhombic system, and have the axial ratios $a : b : c = 0{\cdot}5704 : 1 : 0{\cdot}8283$. M. Oswald gave for the sp. gr. 4·542; and P. C. Ray, 4·453. N. S. Kurnakoff and S. F. Schemtschuschny found that the press. at which the salt begins to flow is 46·6 kgrms. per sq. cm.—tin, 10·5 kgrms. per sq. cm. H. Hess said that the crystals blacken when exposed to light; J. L. Proust, that they darken in air, forming silver and silver nitrate; and N. W. Fischer that they decompose in contact with organic matter—*e.g.* paper. A. Fock said that the salt may be heated for an hour between 100° and 120° without decomposing, and J. Lang found that the air-dried salt does not lose weight at 100°, but decomposition begins at 140°–150°; on the other hand, M. Oswald found that the salt begins to break down at 60°. V. Kohlschütter and E. Eydmann said that the salt decomposes in vacuo in very much the same way as in a current of carbon dioxide. Nitrous fumes can be seen at 150° ; and at 200°, the mass begins to sinter and melt, and soon afterwards so much silver nitrate is formed that the whole mass becomes fluid. E. Péligot said that the decomposition products are silver, silver nitrate, and nitrogen peroxide ; E. Divers said that in an open vessel, the heated nitrite reacts : $3AgNO_2=N_2O_3+2Ag+AgNO_3$; and in a covered crucible : $2AgNO_2=Ag+NO+AgNO_3$; and in moist air, or in water-vapour : $AgNO_2=Ag+NO_2$. M. Oswald said that when heated quickly in vacuo, the salt decomposes : $AgNO_2=Ag+NO_2$. There are, however, some simultaneous reactions : $Ag+2NO_2=NO+AgNO_3$; and $AgNO_2+NO_2=AgNO_3+NO$. R. Abegg and H. Pick represent the decomposition of silver nitrite in aq. soln. by $2AgNO_2 \rightleftharpoons Ag+NO+AgNO_3$, or, on the ionic theory, $Ag^{\cdot}+2NO'_2 \rightleftharpoons Ag+NO+NO'_3$, and the equilibrium press., p, of the nitric oxide is 4·28 atm. at 55°, and 6·29 atm. at 65°. Equilibrium is obtained in 10–14 days. The press. of the nitric oxide is depressed by the addition of potassium nitrite such that for $0{\cdot}25N$-KNO_2, the press., p, is 3·65 atm. at 55°. For the equilibrium condition $K[Ag^{\cdot}][NO'_2]^2=p[NO'_3]$, $K=0{\cdot}000019$; the free energy of the reaction at 55° is $RT \log k=0{\cdot}34$ volt, in agreement with the e.m.f. of the cell Ag | N-Ag, N-NO'_3, N-NO'_2, NO(atm. press.) | Pt which is 0·34 volt. M. Berthelot gave for the heat of formation (Ag,N,O_2) =11·3 Cals. P. C. Ray and N. R. Dhar found the electrical conductivities for dilutions of a mol. of salt in 70·6, 211·8, and 635·4 litres are respectively 70·32, 85·73, and 110·32 at 20°, when the calculated value for infinite dilution is 115·2. A. A. Groening and H. P. Cady measured the decomposition voltages in aq. and in ammoniacal soln.

E. Mitscherlich said that 100 parts of cold water dissolve 0·83 part of silver nitrite, while N. W. Fischer gave less than half this value ; J. Lang said that it is less soluble than silver sulphate. E. Mitscherlich said the solubility increases in hot water, and J. Lang added that the soln. is then partially decomposed. A. Naumann and A. Rücker gave 3·1833 grms. per litre for the solubility of silver nitrite in water at 18°. H. J. M. Creighton and W. H. Ward gave for the solubility, S, in grams per litre :

	0°	10°	15°	20°	25°	30°	40°	50°	60°
S .	1·55	2·20	2·75	3·40	4·14	5·00	7·15	9·95	13·63

The measurements of R. Abegg and H. Pick are rather higher than these values for temp. below 20°. The results are in agreement with single determinations by H. Ley and K. Schäfer, and S. von Niementowsky and J. von Roszkowsky. R. Abegg and H. Pick found the conc. of the silver ions in a sat. soln. of silver nitrite to be 0·0146 at 25°, and the degree of ionization, 55 per cent. H. Ley and K. Schäfer's conductivity measurements gave for the degree of ionization, 59 per cent., and of the solubility product, $[Ag^{\cdot}][NO_2]$, 0·0002. The addition of silver nitrate lowers the solubility of silver nitrite in accord with the theory of the effect of like ions. The solubility of silver nitrite in aq. soln. of silver nitrate was measured by A. Naumann and A. Rücker, R. Abegg and H. Pick, and H. J. M. Creighton and W. H. Ward. The last-named workers found at 25°, with conc. expressed in mols per litre :

$AgNO_3$ . .	0	0·00258	0·00588	0·01177	0·02355	0·04710
$AgNO_2$ . .	0·0269	0·0260	0·0244	0·0224	0·0192	0·0164

The presence of potassium nitrite raises the solubility of silver nitrite ; the effect of like ions being here marked by the formation of a complex. Measurements were made by H. J. M. Creighton and W. H. Ward, who found

KNO_2 . . .	0	0·00258	0·00588	0·01177	0·02355	0·04710
$AgNO_2$ . .	0·0269	0·0259	0·0249	0·0230	0·0203	0·0181

Observations made by R. Abegg and H. Pick indicate the formation of complex univalent $Ag(NO_2)_2$-ions. M. Oswald's curves are shown in Fig. 81, and they are consonant with the formation of a salt $KAg(NO_2)_2$. The ionization constant $k_1=0{\cdot}00068$, for $Ag^{\cdot}+2NO_2 \rightleftharpoons Ag(NO_2)'_2$, or $k_1[Ag^{\cdot}][NO'_2]^2=[Ag(NO_2)'_2]$; and

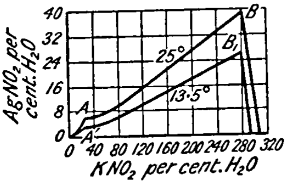


FIG. 79.—Solubility Curves of Silver and Potassium Nitrites.

$k_2=0{\cdot}052$, for $k_2[NO'_2][AgNO_2]=[Ag(NO_2)'_2]$. Calculations show that in a sat. soln. of silver nitrite, at 25°, the conc. of the $Ag(NO_2)'_2$-ions is 0·0017 mol per litre; $Ag^{\cdot}$-ions, 0·0146 mol per litre; NO'_2-ions, 0·0129 mol per litre; and non-ionized $AgNO_2$, 0·0119 mol per litre. The reduction potential of silver nitrite: $2NO'_2=NO+NO'_3$ is 0·43 volt at 25°, when the potential of the hydrogen electrode is zero. This means that when the substances taking part in the equilibrium are present in unit conc., the nitrite ion is 0·43 volt less powerful a reducing agent than hydrogen. The reducing action of the nitrite-ion is greatly increased when the conc. of the nitric oxide is small. N. R. Dhar and D. N. Bhattacharyya observed a brown film is formed on the silver electrode during the electrolysis of a soln. of silver nitrite. According to H. Pick, *oxygen* of the air rapidly oxidizes a soln. of silver nitrite, and the reaction is accelerated by the presence of finely-divided silver. The reaction begins at about 25°, and at 40°, nitric oxide is given off. J. Krutwig found that *chlorine* reacts with silver nitrite, forming nitrosyl chloride, silver chloride, and nitrogen peroxide; and W. Neelmeier, that *iodine* in different solvents, forms silver iodide and nitrogen peroxide. H. Hess showed that *hydrochloric acid* converts the nitrite into the chloride, with the evolution of gas; and E. Mitscherlich obtained silver chloride and alkali nitrites, when a soln. of alkali chloride is treated with silver nitrite. E. Divers and T. Haga showed that if suspended in water, silver nitrite reacts with *hydrogen sulphide*, forming sulphur, nitric oxide, ammonia, and hydroxylamine; and with an excess of *sulphur dioxide*, silver sulphite, sulphuric acid, and nitric oxide are formed. E. C. Franklin and C. A. Kraus found silver nitrite to be readily soluble in liquid *ammonia;* and likewise, also, J. Lang, and H. Hess, in aq. ammonia. E. Mitscherlich, A. Fock, and A. Reychler found that the soln. of silver nitrite in warm, conc. aq. ammonia deposits crystals of **silver amminonitrite,** $AgNO_2.NH_3$, on cooling. A. Reychler dried the yellow crystals with filter-paper, washed them with alcohol and ether, and then exposed them to dry air. According to A. Fock, the yellow prisms belong to the tetragonal system, and have the axial ratio $a:c=1:0{\cdot}6086$. A. Reychler said the m.p. is 70°, and the molten mass crystallizes on freezing. The salt is sparingly soluble in water, less soluble in alcohol, and almost insoluble in ether. The soln. gradually gives off ammonia, and the same gas is given off during fusion. Ethyl iodide reacts: $AgNO_2.NH_3+C_2H_5I=AgI+C_2H_5NO_2+NH_3$. A. Reychler made **silver diamminonitrite,** $AgNO_2.2NH_3$, by shaking the powdered monammine with alcohol sat. with ammonia. Ether added to the filtered soln. precipitates the white salt, which cannot be dried without losing ammonia. It is hygroscopic. The powdered monammine also absorbs ammonia with the evolution of heat and forms **silver triamminonitrite,** $AgNO_2.3NH_3$, which is very soluble in water, and gives off ammonia when exposed to air. According to C. Paal, when silver nitrite acts on hydroxylamine chloride, hydroxylamine nitrite is formed which immediately breaks up into silver hyponitrite. If an excess of silver nitrite be employed, the filtered soln. deposits crystals of **silver dinitritohyponitrite,** $Ag_2N_2O_2.2AgNO_2$. E. Divers has questioned the individuality of the alleged complex. H. Pellet found the nitrite is decomposed by *nitric acid.* E. Divers and T. Shimidzu observed no reaction with *nitrogen peroxide;* C. Paal found that *hydroxylamine chloride* furnishes hydroxylamine nitrite (*q.v.*); and A. Angeli, that *hydrazine sulphate* forms silver azide. L. Kahlenberg and J. V. Steinle represented the reaction with arsenic: $6AgNO_2+2As=As_2O_3+6Ag+3NO_2+3NO$. P. Pistschimuka found that *alkyl thiophosphates* react with silver nitrite as they do with silver nitrate. F. Bezold observed that silver nitrite is sparingly soluble in *methyl acetate;* M. Hamers, insoluble in dry *ethyl acetate,* or in ethyl acetate sat. with water at 18°; and R. Scholl and W. Steinkopf, that 100 parts of *acetonitrile* at ordinary temp. dissolve about 23 parts of silver nitrite, and at 81·6°, 40 parts, and the hot soln. on cooling deposits needle-like crystals of silver nitrite. The action of *alkyl iodides* has been discussed in connection with the constitution. N. W. Fischer found that if an aq. soln. of silver nitrite is free from the nitrate, in the absence of air, it is not reduced by *tin, antimony, bismuth,* or *nickel,* but if silver nitrate is present, reduction occurs.

G. S. Jamieson prepared **cæsium silver nitrite,** $CsNO_2.AgNO_2$, in lemon-yellow hemimorphic crystals from a hot soln. of 10 mols of cæsium nitrite and one mol of silver nitrite. The effect of potassium nitrite on the solubility of silver nitrite has been already discussed—Fig. 79. The zone of stability of the double salt is in the regions *AB,* and *A′B′*. N. W. Fischer, and J. Lang made **potassium silver nitrite,** $KNO_2.AgNO_2.\frac{1}{2}H_2O$, by crystallization from a soln. of the constituent salts with an excess of potassium nitrite, by evaporation at 30°–40°, or over conc. sulphuric acid; and W. Hampe by saturating a conc. soln. of potassium nitrite with silver nitrite at 60°–70°, and evaporating at ordinary temp. in darkness. A. Fock said that the salt is anhydrous, and that the bipyramidal crystals belong to the rhombic system, and have the axial ratios $a : b : c = 0·52751 : 1 : 1·9883$. M. Oswald also found the salt is anhydrous after drying in vacuo in the cold over phosphorus pentoxide. The sp. gr. of the solid is 2·868 at 0°/0°. N. W. Fischer said that the salt is stable in air, but decomposes when heated with its components, and at a higher temp. the silver nitrite breaks down; water extracts the alkali nitrite, leaving the silver nitrite. M. Oswald found that the salt decomposes in vacuo at 100°. J. Lang found that the salt dissolves completely in a small proportion of water, but is decomposed by a large proportion. The salt dissolves unchanged in a soln. of potassium nitrite, but not in alcohol. M. Oswald examined the effect of sodium nitrite on the solubility of silver nitrite, and obtained the results shown in Fig. 80. A complex hemihydrated **sodium silver nitrite,** $NaAg(NO_2)_2.\frac{1}{2}H_2O$, is formed from a soln. of two parts of sodium nitrite in three parts of water, and adding as much silver nitrite as the soln. will dissolve at 50°–60°. The filtered soln. gives crystals of the salt. The zone of stability of the double salt is *AB,* and *A′B′*. The sp. gr. is 3·442 at 0°/0°. The effect of lithium nitrite on the solubility of silver nitrite is shown in Fig. 81. There is no evidence of the formation of *lithium silver nitrite.*

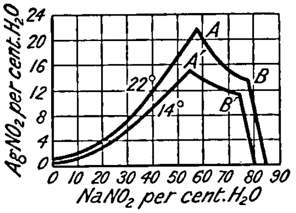


FIG. 80.—Solubility of Silver Nitrite in Solutions of Sodium Nitrite.

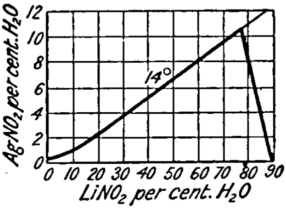


FIG. 81.—Solubility of Silver Nitrite in Solutions of Lithium Nitrite.

N. W. Fischer,[5] J. Lang, and W. Hampe prepared **calcium nitrite,** $Ca(NO_2)_2.H_2O$, by treating a boiling soln. of silver nitrite with calcium hydroxide, and removing the excess of silver by hydrogen sulphide, or the excess of calcium hydroxide by carbon dioxide. J. Lang obtained only a small proportion of calcium nitrite by heating the nitrate. P. C. Ray obtained the salt by the action of silver nitrite on a soln. of calcium chloride. F. Vogel evaporated the filtered soln. to a syrupy consistency and precipitated the salt with alcohol, washed the product a number of times with alcohol, and then dried it at 50°. N. W. Fischer obtained **strontium nitrite,** $Sr(NO_2)_2.H_2O$, by calcining the nitrate and crystallizing out the nitrate from the aq. soln. of the residue. M. Oswald also obtained tetrahydrated calcium nitrite, $Ca(NO_2)_2.4H_2O$; and the conditions of equilibrium are indicated in Fig. 82, but, added J. Lang, it is then very difficult to eliminate the undecomposed nitrate. W. Hampe used the process for the barium salt—*vide infra;* and

F. Vogel treated a soln. of silver nitrite with strontium chloride, evaporated the filtered soln. to a syrupy consistency, and added alcohol as in the case of the calcium salt. H. Hess prepared **barium nitrite,** $Ba(NO_2).H_2O$, by calcining the nitrate; digesting the mass in water; and crystallizing. He called the product *Stickstoffoxydbaryt.* J. Lang, and N. W. Fischer dissolved the calcined residue in water, crystallized out undecomposed barium nitrate, and precipitated any barium hydroxide by passage of carbon dioxide; the addition of a little alcohol precipitated crystals of barium nitrate, and afterwards flecks of the nitrite appeared. The soln. was then allowed to crystallize, and any nitrite in the residue precipitated by alcohol. Neither K. Arndt, nor P. C. Ray could recommend the process. J. Fritzche saturated a soln. of barium hydroxide with the red vapours evolved when fuming nitric acid is heated, and, after evaporating to dryness, extracted the mass with a little water to remove barium nitrate—barium nitrite remains. W. Hampe used barium carbonate suspended in water in place of barium hydroxide; and the conc. soln. remaining after barium nitrate has crystallized out, was treated with 90 per cent. alcohol; and the filtered soln. evaporated for the nitrite. K. Arndt did not recommend this mode of preparation. C. F. Rammelsberg, and P. C. Ray obtained barium nitrite by double decomposition with silver nitrite and barium chloride. K. Arndt recommended mixing the silver nitrite with sea-sand before adding it to the barium chloride soln. J. Matuschek obtained barium nitrite by the double decomposition of barium chloride and sodium nitrite, and fractional crystallization. O. N. Witt and K. Ludwig employed the following process:

> Eq. quantities of dry sodium nitrite and barium chloride are intimately mixed and added to sodium nitrite (1 eq.) dissolved in 3 times its wt. of boiling water. By using an excess of sodium nitrite, the "salting out" of part of the barium chloride before the reaction is complete is prevented. The precipitated sodium chloride is immediately removed by a hot filter, and on cooling the filtrate, well-defined crystals of barium nitrite, $Ba(NO_2)_2,H_2O$, are obtained. They are best removed by the aid of a good centrifuge. The mother-liquor, which contains the excess of sodium nitrite, may be used again. When heated, it begins to evolve oxides of nitrogen at 115°.

W. Meyerhoffer said that under the conditions here described, the salt pair, barium nitrite and sodium chloride, is stable within its interval of change, and that in the presence of water it will separate as a third salt, while barium chloride and sodium nitrite will remain in soln. To prevent this an excess of sodium nitrite is necessary. J. Matuschek showed that hydrated barium chloride and sodium nitrite interact when pounded together, and that these salts react in molecular proportion in aq. soln. at 100° if only a limited amount of water is present. The yield of barium nitrite approaches the theoretical when the amount of water added as solvent is one-third of the weight of the nitrite which would be formed if the reaction were quantitative.

M. Oswald noted the tendency of the salts to form supersaturated soln., and he obtained yellow glasses by cooling the soln. to —80°. Calcium nitrite, according to F. Vogel, forms six-sided prismatic needles which are isomorphous with the barium salt; W. Hampe described the crystals of strontium nitrate as acicular when produced by cooling the hot soln.; but octahedral, if obtained by evaporating the aq. soln. at 90°. M. Oswald found the monohydrates of barium and strontium nitrites to be isomorphous—this merits further examination. A. Eppler said the crystals belong to the cubic system. F. Vogel found barium nitrite furnishes six-sided prismatic crystals which, according to A. Fock, belong to the hexagonal system and have the axial ratio $a : c = 1 : 2{\cdot}5056$. M. Oswald gave 1·674 at 0°/0° for the tetrahydrated calcium salt; 2·408 at 0°/0° for the monohydrated strontium salt; and 3·109 at 0°/0° for the monohydrated barium salt. K. Arndt gave 1·1140 for the sp. gr. of a soln. with 150·005 grms. of barium nitrite per litre; and F. Vogel, for a soln. sat. at 0°, sp. gr. 1·40; at 20°, 1·45; at 25°, 1·50; at 30°, 1·52; and at 35°, 1·61. M. Oswald found that the aq. soln. of calcium nitrite, sat. at 16°, has a sp. gr. 1·4205 at 16°/0°, and contains 42·3 per cent. $Ca(NO_2)_2$; the soln. of the strontium salt, sat. at 19°, has a sp. gr. 1·4461 at 19°/0°, and has 39·3 per cent. $Sr(NO_2)_2$; and the soln. of barium nitrite sat. at 17°, has a sp. gr. 1·4897 at 17°/0°, and has 40 per cent. of $Ba(NO_2)_2$. The sat. soln. of strontium nitrite boils at 112·5° and 763 mm., and of barium nitrite, at 114° and 769·5 mm. The crystals of calcium nitrite are deliquescent, but, according to O. N. Witt and K. Ludwig, those of barium nitrite are not hygroscopic; and, added K. Arndt, the crystals usually contain a little less water than is required for the monohydrate, owing to effervescence. A. Fock considered the salt to be anhydrous. J. Lang and F. Vogel said that the crystals of strontium nitrite are stable in dry air, hygroscopic in moist air. P. C. Ray said that calcium nitrite, dried in a desiccator, and then on a water-bath to constant weight, is hemihydrated, $Ca(BO_2)_2.\frac{1}{2}H_2O$; J. Lang, W. Hampe, and F. Vogel said the crystals are monohydrated; M. Oswald showed that both monohydrated and tetrahydrated calcium nitrite can be formed, and that the transition temp. is 44°, Fig. 82. According to F. Vogel, calcium nitrite at 40° loses 3·1 per cent. of its water of crystallization, and at 100° all is lost. The dehydrated salt absorbs from atm. air at ordinary temp. 14·83 per cent. of water. The monohydrated strontium salt does not lose any water of crystallization, but all is given off above 100° with a slight decomposition. All the water is restored by a few days' exposure to atm. air. Similarly, the barium salt loses its 7·28 per cent. of water of crystallization below 100°, and after 20 days' exposure to atm. air, 3·10 per cent. has been restored. O. N. Witt and K. Ludwig found that the decomposition of the barium salt begins at about 115° so that the water has to be determined by the methods of organic analysis; conc. soln. boiling over 115° decompose, but dil. soln. are quite stable. M. Oswald found that the temp. at which the salts begin to decompose are 220° for calcium nitrite; 240° for strontium nitrite; and 235° for barium nitrite. According to P. C. Ray, when barium nitrite is slowly heated nitric oxide is the main product of the reaction, and a portion of the salt is converted into nitrate, $3Ba(NO_2)_2=2BaO+Ba(NO_3)_2+4NO$, with the side reaction $2Ba(NO_2)_2=BaO+Ba(NO_3)_2+NO+N$; in the second stage, the nitrate decomposes, giving off oxygen: $Ba(NO_3)_2=BaO+2NO_2+O$, and $Ba(NO_3)_2=Ba(NO_2)_2+O_2$. There are also a number of other reactions proceeding simultaneously; thus, M. Oswald found at 150°: $Ba(NO_2)_2+2NO_2=Ba(NO_3)_2+2NO+19{\cdot}6$ Cals.; and $Ba(NO_2)_2+NO_2=Ba(NO_3)_2+N+55{\cdot}2$ Cals. P. C. Ray said that calcium nitrite decomposes like the barium salt. K. Arndt gave 220° for the m.p. of barium nitrite, and M. Oswald, 217°. M. Berthelot measured the heat of formation of barium nitrite and obtained $(Ba,N_2,2O_2)=179{\cdot}6$ Cals. E. C. C. Baly and C. H. Desch measured the absorption spectrum of barium nitrite —*vide infra*, the action of nitrogen peroxide on calcium oxide.

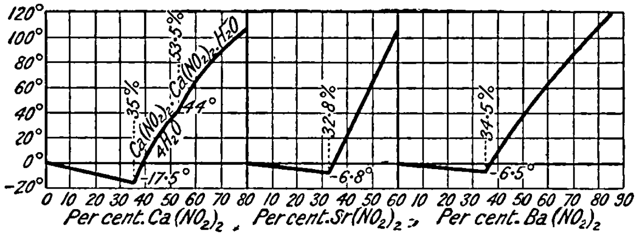


FIG. 82.—Solubility of Calcium Nitrite.

FIG. 83.—Solubility of Strontium Nitrite.

FIG. 84.—Solubility of Barium Nitrite.

F. Vogel found that 100 c.c. of an aq. soln. of calcium nitrite has 111·6 grms. of the monohydrate. M. Oswald's solubility curves are indicated in Fig. 82. The eutectic occurs at —17·5° and 35 per cent. $Ca(NO_2)_2$. The percentage solubility, *S*, is:

	−9·5°	0°	18·5°	42°	44°	54°	64°	70°	91°
S . .	36·2	28·3	43·0	51·8	53·5	55·2	58·4	60·3	71·2
Solid phase	$Ca(NO_2)_2.4H_2O$					$Ca(NO_2)_2.H_2O$			

At higher temp., the salt is much hydrolyzed. W. Hampe, and J. Lang noted that strontium nitrate is very soluble in water, and F. Vogel found that 100 c.c. of a soln. at 19·5° has 62·83 grms. of $Sr(NO_2)_2.H_2O$; while M. Oswald obtained the results indicated in Fig. 83. The eutectic at —6·8° has 32·8 per cent. $Sr(NO_2)_2$. For the solubility, *S*, of monohydrated strontium and barium nitrites, per 100 parts of water, M. Oswald gave:

S	0°	10°	20°	40°	60°	80°	100°	110°
$Sr(NO_2)_2.H_2O$	58·9	67·6	75·5	94	116	145	182	—
$Ba(NO_2)_2.H_2O$	63·5	69·5	79·5	113	170	254	461	765

J. Lang, and W. Hampe found barium nitrite to be very soluble in water, and F. Vogel measured the solubility between 0° and 35°. M. Oswald's results are indicated above and in Fig. 84. The eutectic is at —6·5°, with 34·5 per cent. $Ba(NO_2)_2$. There are no hydrates other than the monohydrates of barium and strontium nitrites. J. Lang said that the aq. soln. of barium nitrite is feebly alkaline, but W. Hampe, and K. Arndt observed the soln. has no action on litmus unless the salt has been previously evaporated to dryness with consequent decomposition. According to M. Oswald, the hydrated nitrites can be dehydrated in a vacuum over phosphoric oxide without undergoing decomposition; in conc. aq. soln. lithium nitrite and the alkaline-earth nitrites undergo hydrolysis at 100°. The solid nitrites or their sat. soln. are not oxidized by oxygen at atmospheric pressure, neither are the dry salts acted on by nitric oxide, so long as decomposition of the salt itself does not occur. Oxidation of soln. of the nitrites occurs only in the presence of acids, and is then due to oxidation of the decomposition products (nitric oxide) of nitrous acid. F. Vogel gave for the eq. conductivity, λ, aq. soln. with the conc. expressed in gram-eq. per litre, at 25°:

Conc. . .	5·0	3·0	2·5	2·0	1·0	0·1	0·05	0·01	0·005	∞
$Ca(NO_2)_2$ . .	—	—	45·5	51·2	66·4	96·0	103	116	120	124
$Sr(NO_2)_2$ . .	23·9	40·8	46·0	51·8	67·6	99·0	105	120·4	121	125
$Ba(NO_2)_2$ . .	—	40·3	45·5	51·3	66·4	99·0	105	114	115	122

P. C. Ray and N. R. Dhar also measured the electrical conductivities of soln. of the three nitrites; and P. C. Ray and S. C. Mukherjee observed that the degrees of ionization of soln. of calcium nitrite at dilutions $v=28·0$ and 19·4 litres are respectively 0·84 and 0·82; for strontium nitrite at dilutions $v=22·0$ and 21·0 litres, 0·84 in both cases; and for barium nitrite for $v=21·0$ and 31·4 litres, respectively 0·84 and 0·86.

N. W. Fischer said that calcium nitrite is insoluble in dil. alcohol, and F. Vogel, that 100 c.c. of 90 per cent. alcohol dissolve 39·0 grms. of the salt. at 20°, and 100 c.c. of absolute alcohol, 1·1 grms. W. Hampe, and J. Lang found that strontium nitrite is sparingly soluble in absolute alcohol, and F. Vogel showed that 100 c.c. of 90 per cent. alcohol, at 19·5°, dissolve 0·42 grm. of salt, and 100 c.c. of absolute alcohol, 0·04 grm. J. Lang, and W. Hampe said that barium nitrite is nearly insoluble in absolute alcohol; and F. Vogel found that 100 c.c. of alcohol and water, at 19°–21°, dissolve *S* grms. of monohydrated barium nitrite:

Alcohol .	10	20	30	40	50	60	70	80	90	100 per cent.
Ba salt .	49·30	29·30	18 41	13·33	9·11	4·84	2·66	0·98	0·00	0·00

According to E. C. Franklin and C. A. Kraus, a soln. of barium nitrite in liquid ammonia reacts with the following salts dissolved in liquid ammonia—ammonium chloride, bromide, and iodide are precipitated; ammonium chromate gives a flocculent precipitate; and ammonium borate also gives a precipitate. C. Matignon and E. Monnet observed that the oxidation of solid calcium nitrite to nitrate can be effected as in the case of sodium nitrite (*q.v.*) by heating it in oxygen under press.

J. Lang, and A. Fock prepared **potassium calcium nitrite,** $KNO_2.Ca(NO_2)_2.3H_2O$, by slowly evaporating a soln. of the component salts. J. Lang obtained **potassium strontium nitrite,** $2KNO_2.Sr(NO_2)_2$, and **potassium barium nitrite,** $2KNO_2.Ba(NO_2)_2$, in an analogous way. J. Lang also claimed to have made the monohydrate, $2KNO_2.Ba(NO_2)_2.H_2O$, in long, acicular crystals stable in air; easily soluble in water, but not in alcohol; and dehydrated at 100°—but A. Fock did not verify this result. H. Topsöe described the crystals of the calcium salt as colourless, rhombic, bipyramidal prisms with the axial ratios $a:b:c=0·642:1:0·642$; and A. Fock said that the crystals of the pseudohexagonal prisms of the barium salt are rhombic with axial ratios $a:b:c=0·5832:1:—$. A. Fock found that the crystals of the barium salt preserve their lustre when heated many hours at 120°, but at 150°, they slowly lose their lustre. J. E. Ahlen said that the calcium salt is dehydrated at 100°. W. N. Fischer reported **silver barium nitrite,** $BaAg_2(NO_2)_4.H_2O$, from a soln. of the component salts. The formula is here due to M. Oswald, who examined the three nitrites of the alkaline earths, and found only barium forms a double salt. The conditions of stability are represented by *AB*, Fig. 85. The corresponding diagrams for strontium and calcium nitrites do not show any evidence of the formation of *silver strontium nitrite*, or of a *silver calcium nitrite;* nor is any *strontium barium nitrite* formed, for the two salts give a series of mixed crystals, $(Ba,Sr)(NO_2)_2.H_2O$.

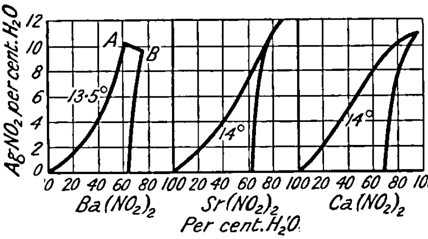


FIG. 85.—Binary System: $Ba(NO_2)_2-AgNO_2$.

FIG. 86.—Binary System: $Sr(NO_2)_2-AgNO_2$.

FIG. 87.—Binary System: $Ca(NO_2)_2-AgNO_2$.

C. Przibylla obtained a series of triple nitrites; thus, **copper calcium potassium nitrite,** $CuCaK,(NO_2)_6$, prepared by mixing a well-cooled soln. of copper chloride and sodium nitrite with a soln. of potassium chloride, calcium chloride, and sodium nitrite, is a deep green, crystalline powder, which is purified by washing with 85 per cent. alcohol and then with alcohol. **Copper calcium ammonium nitrite,** $CuCa(NH_4)_2(NO_2)_6$, prepared in a similar manner to the preceding salt but using very conc. soln., closely resembles the potassium salt, but if kept, gradually decomposes with evolution of nitrogen trioxide. **Copper barium potassium nitrite,** $CuBaK_2(NO_2)_6$, obtained by mixing a well-cooled conc. soln. of barium chloride and sodium nitrite with a soln. of copper chloride, potassium chloride, and sodium nitrite, is also a deep green, crystalline powder; it is stable when kept dry, but decomposes on recrystallization, with evolution of nitrogen trioxide and the formation of basic salts. **Copper barium ammonium nitrite,** $CuBa(NH_4)_2(NO_2)_6$, is very similar to the potassium salt, but slowly decomposes when allowed to remain at the ordinary temperature. **Copper strontium potassium nitrite,** $CuSrK_2(NO_2)_6$, is obtained in a similar manner to the preceding salts, but a large excess of strontium chloride should be employed, as otherwise a mixture of salts is obtained containing less strontium; these cannot be purified by recrystallization. The corresponding **copper strontium ammonium nitrite** is very similar to the potassium salt.

F. Vogel tried without success to make **beryllium nitrite** by the action of beryllium sulphate on barium nitrite. He found that in aq. soln. the precipitate is immediately hydrolyzed, nitrogen oxides are evolved, and only a small proportion of nitrogen remains. It might be added that many salts, unstable in aq. soln., have been made in non-aq. solvents. D. B. Q. Disjonval prepared **magnesium nitrite,** presumably $Mg(NO_2)_2$, by the action of nitrous acid on magnesium hydroxide. J. Lang, W. Hampe, and P. C. Ray obtained it by double decomposition between magnesium sulphate and sodium nitrite and magnesium sulphate, and fractional crystallization—*vide supra,* barium nitrite; and L. Spiegel, by digesting at 50°–60° a mixture of silver nitrate and magnesium chloride; removing the silver from the filtrate by hydrogen sulphide; and evaporating the filtrate first on the water-bath, and finally over sulphuric acid. P. C. Ray said that the soln. should not be evaporated on the water-bath because of its ready hydrolysis; it is best conc. under reduced press. over sulphuric acid. L. Spiegel, J. Matuschek and W. Hampe found the salt dried over sulphuric acid is dihydrated; and L. Spiegel, J. Lang, and F. Vogel prepared a trihydrated salt. The white thin plates, or prismatic columns, are deliquescent. J. Lang said that they decompose at 100°, giving off nitric oxide, and so also with the aq. soln. L. Spiegel said that the crystals cannot be dried to constant weight since a little decomposition also occurs; a marked decomposition occurs at 97°–100°, but the soln. can be boiled a long time without perceptible decomposition. F. P. Dunnington and F. W. Smither said that all but one mol of water can be driven from the salt at 97°–100°, but any further loss of water is attended by a loss of acid. According to P. C. Ray, the salt spontaneously decomposes in a sealed vessel, giving off red fumes. If heated in vacuo, the salt decomposes like barium nitrite (*q.v.*). The decomposition begins at 60°, and at 120° a basic nitrate, $MgO.Mg(NO_3)_2$, is formed which is stable at 175°. F. Vogel made analogous observations. P. C. Ray and R. R. Dhar found the electrical conductivities of soln. with a mol of the salt in 15·5, 46·5, 139·5, and 418·5 to be respectively 91·15, 108·65, 120·55, and 127·15 at 20°, and at infinite dilution, 106·9. W. Hampe found the salt to be readily soluble in alcohol. J. Lang reported **potassium magnesium nitrite** to be formed in a manner analogous to the corresponding barium salt. A. Reychler reported crystals of **magnesium silver nitrite,** $AgNO_2.19Mg(NO_2)_2.50H_2O$, to be formed from a mixed soln. of the component salts. The complex nitrite is readily soluble in water, and the soln. is rapidly decomposed by light.

According to A. Vogel and C. Reischauer,[6] **zinc nitrite,** $Zn(NO_2)_2$, is formed copiously when zinc dissolves in nitric acid, or in a soln. of zinc hydroxide in aq. ammonia, and in the latter case, crystals of the hydroxide are simultaneously formed. J. Matuschek obtained it by a process analogous to that employed for the barium salt. F. Vogel could not obtain a satisfactory result with J. Matuschek's method. The rhombic plates were **monohydrated zinc nitrite,** $Zn(NO_2)_2.H_2O$. They decompose in air, and, when dissolved in water, form nitrous acid and zinc hydroxide. W. Hampe, and J. Lang said that the conc. soln. is stable, but J. Matuschek found that it gradually forms zinc nitrate and hydroxide. According to P. C. Ray, zinc nitrite cannot be crystallized from the aq. soln., prepared by the double decomposition of a soln. of zinc sulphate and barium nitrite, for the conc. soln. decomposes—even in vacuo—with the evolution of nitric oxide and the formation of a basic nitrate. P. C. Ray and N. R. Dhar gave for the eq. conductivity of a mol of the salt in v litres of water at 20°:

v . . .	12·4	37·2	111·6	334·8	1004·4
λ . . .	59·27	80·87	104·30	116·25	117·65

The calculated value is 108·1 at infinite dilution. The aq. soln. is acidic owing to hydrolysis. By evaporating a soln. of zinc nitrite, W. Hampe obtained plates of **zinc oxynitrite,** $ZnO.Zn(NO_2)_2$. J. Lang obtained **trihydrated zinc nitrite,** $Zn(NO_2).3H_2O$, by evaporating in vacuo the filtered soln. obtained when zinc sulphate has been treated with barium nitrite. The aq. soln. is not precipitated by alcohol. The crystals decompose at 100° giving off nitric oxide. F. Ephraim and E. Bolle obtained a doubtful **zinc amminonitrite** by saturating a soln. of zinc nitrite with ammonia. J. Lang said that yellow, prismatic crystals of

potassium zinc tetranitrite, $2KNO_2.Zn(NO_2)_2.H_2O$, were produced by crystallization from a mixed soln. of the component salts. W. Hampe obtained a similar salt. A. Rosenheim and K. Oppenheim reported pale yellow, very hygroscopic crystals of **potassium zinc pentanitrite,** $3KNO_2.Zn(NO_2)_2.3H_2O$, by adding nitrous acid to a mixture of zinc hydroxide and potassium nitrite, stirred up with water. The crystals are decomposed by water.

F. Vogel prepared crystals of **cadmium nitrite,** $Cd(NO_2)_2$, by evaporating in vacuo the soln. remaining after mixing eq. proportions of barium nitrite and cadmium sulphate in aq. soln. P. C. Ray obtained cadmium nitrite in bright, pale yellow crystals, by triturating a mixture of cadmium chloride and silver nitrite, water being added from time to time, until the filtrate showed no evidence of an excess of either salt. The liquid was then evaporated in vacuo over sulphuric acid. J. Lang obtained hydrated cadmium nitrite, $Cd(NO_2)_2.H_2O$, as a yellow crystalline mass by evaporating the same soln. at as low a temp. as possible. The salt is decomposed by heat, and by water. P. C. Ray found that cadmium nitrite began to decompose at 150°, and at 230°, a brown residue of cadmium nitrate and oxide was formed. Nitric oxide is the chief gaseous product: $3Cd(NO_2)_2=2CdO+Cd(NO_3)_2+4NO$; and there is a side reaction: $Cd(NO_2)_2=CdO+N_2O_3(NO+NO_2)$. The eq. conductivity at 29° with a mol of the salt in v litres of water is:

v . . .	10	20	40	80	160	320	640	1024
λ . . .	33·7	43·9	55·1	67·1	78·3	88·3	96·1	104·6

W. Hampe obtained **cadmium oxynitrite,** $CdO.Cd(NO_2)_2$, as a white, insoluble powder by the action of water or absolute alcohol on the normal salt. According to H. Morin, when a sat. soln. of ammonium nitrate is poured upon granulated cadmium, an energetic reaction takes place with tumultuous ebullition, and the temperature rises to 110°; but there is no evolution of gas. After cooling, the liquid is filtered and allowed to evaporate over calcium chloride out of direct sunlight; it then deposits transparent rhomboidal prisms, which, when dried, do not alter on exposure to air. These crystals are decomposed by water with separation of flocculent cadmium oxide; they can, however, be crystallized from a soln. of ammonia. When heated, they melt and give off ammonia, and as soon as they are completely dry, they decompose with sudden deflagration, nitrogen oxides being given off, and a residue of anhydrous cadmium oxide left. The crystals correspond with **ammonium cadmium diamminoxytetranitrite,** $CdO.Cd(NO_2)_2.2NH_4NO_2.2NH_3.H_2O$. G. Carrara obtained a cadmium nitrite of indefinite composition about a cadmium anode during the electrolysis of a soln. of cadmium nitrate; no ammonia was detected. C. F. Schönbein said that a nitrite is formed when a cadmium rod is left in contact with a soln. of ammonium nitrite for some time. W. Hampe, and A. Fock reported crystals of **potassium cadmium trinitrite,** $KNO_2.Cd(NO_2)_2$, to be formed by evaporating a mixed soln. of the component salts. V. Kohlschütter obtained the salt by adding alcohol to an aq. soln. of the tetranitrite. The soln. first forms pale yellow cubes, or plates. The salt is not changed by recrystallization of the aq. soln. The crystals are stable in air, readily soluble in water, and sparingly soluble in alcohol. The mother-liquor remaining after the preparation of the preceding salt furnishes rhombic prisms of **potassium cadmium tetranitrite,** $2KNO_2.Cd(NO_2)_2$. J. Lang obtained the same salt by the spontaneous evaporation of a soln. of cadmium acetate with a large excess of potassium nitrite; A. Laubenheimer, by evaporating, in vacuo, over sulphuric acid, a soln. obtained by treating silver nitrite with the right proportion of cadmium and potassium chlorides; and V. Kohlschütter, from a conc. soln. of potassium nitrite and cadmium sulphate. According to A. Fock, the pale yellow crystals belong to the rhombic system and have the axial ratios $a:b:c=0·5369:1:1·9237$; H. Topsöe made some observations on this subject. P. Groth said the optic axial ratio is $2E$=c. 80°; and the indices of refraction for Na-light are $\beta=1·565$, and $\gamma=1·608$.

The crystals are readily soluble in water, but not in alcohol. The salt is not changed by boiling with water, and the soln. has a neutral reaction. According to J. Lang, the mother-liquor remaining after the separation of the tetranitrite furnishes rectangular plates of **potassium cadmium hexanitrite,** $4KNO_2.Cd(NO_2)_2$.

The early literature on mercury nitrites is somewhat confused, and difficult to follow. E. Péligot,[7] and J. H. Niemann prepared a soln. of **mercurous nitrite,** $HgNO_2$, by the action of conc. nitric acid on mercurous nitrate. E. Mitscherlich, and J. Lefort obtained a lemon-yellow basic salt by the action of mercury on a hot soln. of mercurous or mercuric nitrate ; it was taken to be mercurous nitrite. P. C. Ray supposed the lemon-yellow crystals were a basic nitrite, but later showed that they are hydroxymercurosic nitrate, $HgO(HO.HgNO_3)(HO.Hg_2.NO_3)$. C. Gerhardt correctly regarded this product as a mercurosic nitrate ; and it can be regarded as a salt of the orthonitric acid of W. N. Hartley. A. Baudrimont said that mercurous nitrite is formed by the action of nitrous acid on mercury, but C. Gerhardt could obtain only the nitrate by working at 0°. In 1860, J. Lang could say that there was no evidence that mercurous nitrite had ever been isolated—if mercurous nitrate be mixed with potassium nitrite, mercury separates and nitric oxide is evolved ; and if the potassium nitrite be in excess, potassium mercuric nitrate is formed. According to P. C. Ray, however, when mercury and dil. nitric acid are left in contact for a long time, the following salts may be formed : mercurous nitrite, $HgNO_2$; mercuric nitrite, $Hg(NO_2)_2$; mercurous nitrate, $HgNO_3.2H_2O$; and six or seven basic nitrates. Analyses show that the successive formation of these salts involves the initial production of mercurous nitrite ; after this the nitrates and basic nitrates appear. He said : Nitrite is the product of the combined action of nitrous and nitric acids 22°–33° on mercury : $2Hg+HNO_2+HNO_3=2Hg(NO_2)_2+H_2O$. Some of the nitrite is decomposed by the nitric acid, and the quantity of nitrous acid thus rapidly grows until mercurous nitrite and nitrate are accumulating in mol. proportions. Thereafter, the proportion of nitrous acid in soln. remains constant ; and it has become the catalytic agent between nitric acid and mercury which now interact : $2Hg+2HNO_3=HgNO_2+HgNO_3+H_2O$. At lower temp., the effects of diffusion and crystallization were enough to mask the equal production of nitrite and nitrate. When mercury is covered with nitric acid sp. gr. 1·11/15°, to a depth of 10 cms. at 30°–35°, the bright yellow mercurous nitrite soon begins to crystallize, generally as a crust over the mercury, but sometimes in separate large crystals. The whole may be left undisturbed for about 50 hours without the crystals showing erosion. Very little nitric oxide forms on the mercury, and even that is soon absorbed by the soln. In 24 hrs., the soln., just over the mercury, has attained a sp. gr. of 1·6–1·7, whilst at the surface its sp. gr. is hardly altered, scarcely any mercury salts being present. Mercurous nitrite is always formed when nitric acid, with 10–23 per cent. N_2O_5, acts on mercury at 22°–33° ; and an acid containing 13–14 per cent. N_2O_5, corresponding with a 1 : 4 dilution of nitric acid of sp. gr. 1·410, is the most favourable for the production of crystals of mercurous nitrite. If an acid of sp. gr. 1·135–1·140 is used in place of an acid of sp. gr. 1·11, small crystals appear in two or three days along with those of mercurous nitrate ; these soon give way to a crystalline crust, or large isolated crystals of $HgNO_3.H_2O$. The more conc. acid thus converts some nitrite into nitrate. N. R. Dhar found that the conversion of mercury into nitrite is favoured by ferric nitrite ; P. C. Ray found the converse.

P. C. Ray said that the crystals of mercurous nitrite are sulphur-yellow. The sp. gr. is 5·925, and the mol. vol. 83·04. He said that the salt develops nitric oxide at 100°, but P. C. Ray and A. C. Ghosh found that the decomposition begins at 140°, and is completed at 247°. When a thin layer of the nitrite is heated in vacuo, to 195°, P. C. Ray and J. N. Sen did not obtain a complete decomposition, and estimated that that would require a temp. of 250°. They consider that the results of the analysis of the decomposition products are in agreement with E. Divers and T. Shimidzu's observations on the thermal decomposition of silver nitrite, the primary reaction: $2HgNO_2 = 2Hg + 2NO_2$, followed by: $4NO_2 + 2Hg = 2HgNO_3 + 2NO$. Since P. C. Ray has shown that mercurous nitrite, like silver nitrite, interacts with ethyl iodide producing both ethyl nitrite and nitroethane, it is assumed that the mercurous nitrite is tautomeric having both the hydroxylic form $HgO \vdots NO$, and the imidic form $Hg \vdots NO_2$. The scission of the molecules is supposed to occur simultaneously in the regions represented by the dotted lines.

P. C. Ray said that mercurous nitrite can be kept in dry atm. *air* for years without change, but if the salt be exposed to moist air, it decomposes slowly, giving off nitric oxide. When dissolved in *water*, mercurous nitrite slowly forms mercuric nitrite and mercury, but about 22 per cent. remains undecomposed at ordinary temp., and forms, with the mercuric nitrite, mercurosic nitrite, $HgNO_2.2Hg(NO_2)_2$. If the mercurous salt be removed from the soln. by the addition of sodium chloride, a sodium mercuric nitrite is formed. On evaporating the aq. soln. of mercurous nitrite, various basic mercurosic nitrates crystallize out. Besides the anhydrous mercurous nitrite just described, P. C. Ray prepared **hemihydrated mercurous nitrite,** $HgNO_2.\frac{1}{2}H_2O$, in lemon-yellow crystals by allowing a somewhat dil. soln. of mercurous nitrite to evaporate spontaneously in a shallow dish for 2 or 3 days. This salt effloresces when kept in a desiccator over conc. sulphuric acid. T. H. Holland found that crystals are triclinic. P. C. Ray said that the action of water is similar to its effect on the anhydrous salt. E. Divers and T. Haga found that *hydrogen sulphide* reacts with mercurous nitrite suspended in water, forming sulphur, nitric oxide, ammonia, hydroxylamine, and mercuric sulphide; and with an excess of *sulphur dioxide,* mercuric sulphide, sulphuric acid, nitric oxide, and mercuric sulphide are formed. According to P. C. Ray, *sulphuric acid* slowly develops nitrous fumes in contact with mercurous nitrite, especially when heated. Mercurous nitrite changes into mercuric nitrite during the action of *dilute nitric acid* on mercury. The hydrolysis of the mercuric nitrite is the source of the basic mercurous nitrates, for the mercuric hydroxynitrite readily reacts with mercurous nitrate reforming mercurous nitrite, and mercuric hydroxynitrate, $HO.Hg.NO_3$. There is a slow escape of nitric oxide during the hydrolysis of mercuric nitrite. So long as any mercury remains, mercuric hydroxynitrate forms with it mercurous hydroxynitrate, $HO.Hg_2.NO_3$, $4HgNO_3 + 3Hg + Hg(NO_2)_2 + 2H_2O = 2NO + 4(HO.Hg_2.NO_3)$. This salt separates only in combination with the normal nitrate. In a few weeks, all the mercurous nitrite disappears, and crystals of mercurous tetrahydroxynitrate, $Hg_{10}(OH)_4(NO_3)_6$, separate out. If the temp. does not exceed 22°, for a time, these crystals are accompanied or preceded by those of mercurous hydroxytrinitrate, $Hg_4(OH)(NO_3)_3$. P. C. Ray showed that cold *concentrated nitric acid* has no immediate action on mercurous nitrite; but, after a few minutes, energetic action sets in. If the mixture is heated immediately after adding the conc. nitric acid, a violent action begins, copious red fumes are given off, and a clear soln. of mercuric salt is obtained. If, after adding conc. nitric acid, a small quantity of water is poured in, action at once commences, nitrous fumes are evolved, and the liquid becomes bluish; at the same time, a few globules of mercury separate, but disappear on warming the liquid, which contains both mercurous and mercuric salts. If, however, the salt be treated with *cold,* dil. nitric acid, the action is very slow, bubbles of gas being given off at intervals; it is only after the action has continued 3 to 4 days that the salt dissolves, and colourless crystals of a basic mercurous nitrate, $3HgNO_3.2HgOH$, or $Hg_5(OH)_2(NO_3)_3$, are deposited. When *potassium nitrite* is added to a soln. of mercurous nitrite, mercury is precipitated, and mercuric nitrite is formed. According to E. Abel, when mercury, mercuric nitrate, and $3N$-HNO_3 are shaken together, the conc. of the mercurous and mercuric salts in soln. are proportional to the conc. of the corresponding ions, and at 25°, the ratio $HgNO_3 : Hg(NO_3)_2$ is nearly constant, 239·5 : 1. This is taken to prove that the two ions have the same valency and that the reaction takes place in accord with $Hg'' + Hg = (Hg{-}Hg)^{\cdot\cdot}$, the mercurous ion consisting of two atoms. Since the reaction with an excess of potassium nitrite and mercurous nitrite is nearly quantitative, most of the mercuric ions pass into non-ionized mercuric nitrite, or into a stable complex; the measurements of H. Ley and H. Kissel, however, show that mercuric nitrite is appreciably ionized in aq. soln. The measurements of R. Abegg and H. Pick show that with mercurous nitrite the complex $Hg(NO_2)_4$-ion is formed. This corresponds with the salt $K_2Hg(NO_2)_4$—*vide infra*. The constant $k=3{\cdot}5\times10^{-13}$ for $[Hg(NO_2)''_4]=k[Hg]^{\cdot\cdot}[NO'_2]$, and therefore this complex is about five times less stable than the corresponding $HgCl''_4$-ion. P. C. Ray found that *sodium nitrite* and mercurous nitrite give a precipitate of mercury, and mercuric nitrite is formed; hot conc. soln. of mercurous nitrite and *silver nitrite* form a precipitate of silver and mercury—there is no loss of nitrogen, which remains entirely in the form of nitrite—in dil. soln. no silver was precipitated; *sodium chloride* precipitates mercurous salts as calomel when added to a soln. containing mercurous and mercuric salts; and P. C. Ray and P. Néogi, and P. Néogi and B. B. Adhicary studied the action of the alkyl iodides —*vide supra.*

J. Lang was of the opinion that normal **mercuric nitrite,** $Hg(NO_2)_2$, could not be prepared; he tried to make it by evaporating the filtered soln. resulting from the interaction of mercuric chloride and silver nitrite, but obtained only a basic salt. P. C. Ray showed that the failure is here due to the decomposition of the mercuric nitrite when evaporated on a water-bath. If conc. in vacuo over sulphuric acid, the normal salt is readily obtained in tufts of fine needles. H. Ley and H. Kissel obtained it in aq. soln. by the action of silver nitrite on an aq. soln. of mercuric chloride. P. C. Ray obtained it by the hydrolysis of mercurous nitrite as indicated above—about 22 per cent. escapes the hydrolysis. He also obtained it among the products of the action of dil. nitric acid on mercury—*vide supra.* If mol. proportions of crystals of silver nitrite and mercuric chloride are rubbed together with water in a mortar, so as to form a paste; shaken up with more water; and then evaporated in vacuo over sulphuric acid, pale, yellow, needle-like crystals of mercuric nitrite are formed. Mercuric nitrite is not stable in dry air; even in vacuo, over sulphuric acid, at ordinary temp., it gives off nitrous fumes, forming a white basic nitrate; the salt may remain for a long time in vacuo without change, but once decomposition has started, it cannot be arrested. The salt fuses with intumescence at 95°, and nitric oxide is at first evolved, and finally reddish-brown fumes appear. It was assumed that at 100°, the mercuric nitrite breaks up in two ways: $Hg(NO_2)_2=HgO+N_2O_3$; and $Hg(NO_2)_2=HgNO_3+NO$. In a general way, P. C. Ray considers that the greater the at. wt. of the element, the more pronounced the colour of the nitrites of the first and second groups in the periodic system. Mercuric nitrite is a pronounced yellow, magnesium nitrite is nearly white; barium nitrite likewise is more yellow than calcium nitrite. When exposed to air, mercuric nitrite slowly liquefies and gives off nitrous fumes; it dissolves only partially even in boiling water, the larger proportion decomposing into mercuric oxide and nitrous acid. The aq. soln. has an acid reaction. H. Ley and H. Kissel, and P. C. Ray and N. Dhar, measured the mol. conductivity, μ, of aq. soln. of normal mercuric nitrite. The latter found at 20° for soln. with a mol in v litres:

v . . .	17	153	459	1377	4131
μ . . .	5·16	10·18	14·13	34·51	83·32

P. C. Ray and S. C. Mukherjee found the degree of ionization to be 0·11 for a mol of the salt in 32 litres. P. C. Ray and N. Dhar found that if the aq. soln. be kept in a closed vessel for some time, some of the mercuric nitrite forms mercurous nitrate and a basic salt is formed; thus in 3 weeks, a soln. of sp. gr. 1·065 contained mercuric : mercurous mercury as 13·7 : 1. P. C. Ray and N. Dhar found that the conductivity measurements of aq. soln. of mercurous nitrite agree with the assumption that a complex $Hg_2(NO_2)'_5$-ion is present; this corresponds with **mercurosic nitrite,** $HgNO_2.2Hg(NO_2)_2$. For a dilution $v=187$, $\lambda=62{\cdot}33$, and when $v=561$, $\lambda=80{\cdot}10$. With dil. soln., hydrolysis occurs. If the aq. soln. be sealed up in an evacuated tube, the salt is not decomposed. When treated with alkali-lye, the solid salt forms mercuric oxide and alkali nitrite; and with sodium sulphate, the aq. soln. does not precipitate mercuric oxysulphate. P. C. Ray and S. C. Mukherjee estimated the degrees of ionization for dilutions $v=64\cdot8$ and $135\cdot2$ litres, respectively 1·82 and 1·77.

The basic mercuric nitrite obtained by J. Lang—*vide supra*—had the composition $3HgO.N_2O_3.H_2O$, and from the work of P. C. Ray, this product was probably a mixture. By evaporating an aq. soln. of mercurous nitrite, P. C. Ray reported that two **mercurosic hydroxynitrites** are formed after the soln. has deposited the triclinic prisms of hemihydrated mercurous nitrite. The next crop of crystals appears as small, orange nodules with the composition $9Hg_2O.4HgO.5N_2O_3.8H_2O$, and afterwards deep yellow clusters of needles or feathery tufts appear, their composition is given as $Hg_2O.2HgO.N_2O_3.2H_2O$. Later on, P. C. Ray showed that these salts are really mercurosic hydroxynitrates respectively, $(HgO)(HO.Hg_2.NO_3)_2$, and $(HgO)(HO.Hg.NO_3)(HO.Hg_2.NO_3)$. After these crystals have deposited, there then appear thin scaly crystals with a faint yellow tint, which, when dried over sulphuric acid, have the composition $12HgO.5N_2O_3.24H_2O$, or **mercuric hydroxynitrite**, $5Hg(NO_2)_2.7Hg(OH)_2.17H_2O$.

J. Lang, C. F. Rammelsberg, and A. Fock prepared what they regarded as **potassium mercuric tetranitrite**, $2KNO_2.Hg(NO_2)_2$, by evaporating the clear yellow soln. obtained by mixing mercuric nitrate with an excess of potassium nitrite, and drying the product in air or at 100°. P. C. Ray obtained it by grinding mercurous nitrite and potassium nitrite to a paste with the least possible quantity of water, adding more water, and evaporating the filtered soln. in vacuo over sulphuric acid. The pale yellow plates and prisms so obtained, according to A. Fock, belong to the rhombic system. They are very soluble in water, and P. C. Ray and N. Dhar found that the mol. conductivity, μ, of soln. with a mol of the salt in v litres of water, at 20°, is :

v .	17	51	153	459	1377	4131
μ . .	180·8	218·0	242·11	271·6	300·0	362·15

and a comparison of the results for the individual salts are in agreement with the assumption that the complex ion $Hg(NO_2)_4''$ is formed. P. C. Ray and S. C. Mukherjee estimated the degrees of ionization for dilutions $v=7\cdot2$ and $60\cdot4$ litres, to be respectively 1·26, and 1·58. J. Lang said that the salt is insoluble in alcohol; the aq. soln. has a neutral reaction, and can be boiled without change; aq. ammonia gives a pale yellow precipitate with the aq. soln., and the colour changes to white on washing. According to A. Rosenheim and K. Oppenheim, this salt is really hydrated **potassium mercuric pentanitrite**, $3KNO_2.Hg(NO_2)_2.H_2O$, which they prepared by treating dry mercuric nitrate with a very conc. soln. of potassium nitrite, filtering off the separated mercuric oxide, and crystallizing. V. Kohlschütter formulates the salt $[Hg(NO_2)_5H_2O]K_3$; and prepared it by allowing a mixture of dry mercuric oxalate and a very conc. soln. of potassium nitrite to stand for some time. P. C. Ray also prepared this salt; and P. C. Ray and S. C. Mukherjee estimated the degree of ionization to be 1·48 for a dilution $v=23$ litres. H. Töpsöe, A. Fock, P. Groth, and A. Sachs have described the prismatic or tabular crystals. The rhombic bipyramids have the axial ratios $a:b:c=0\cdot8671:1:0\cdot7646$, and are feebly doubly refracting; the optic axial angle $2H=92^\circ 40'$ for Li-light; $92^\circ 20'$ for Na-light; and $91^\circ 30'$ for Tl-light. V. Kohlschütter found that the crystals do not lose their combined water in vacuo over sulphuric acid; and do not lose weight when heated for an hour at 100°; they melt at about 125° without decomposition. According to A. Rosenheim and K. Oppenheim, the salt can be recrystallized from water without change; they obtained crystals of **potassium mercuric trinitrite**, $KNO_2.Hg(NO_2)_2$, by evaporating the mother-liquors obtained in the preparation of the preceding salt; and also from aq. soln. of the component salts with a small excess of potassium nitrite. The salt decomposes in aq. soln. P. C. Ray and J. N. Rakshit made sodium mercuric nitrite, without studying its composition; and P. C. Ray obtained **sodium mercuric**

heptanitrite, $3NaNO_2.2Hg(NO_2)_2$, by rubbing a mixture of mercurous nitrite and sodium nitrite in a mortar using as little water as possible; adding more water; and evaporating the filtered soln. in vacuo over sulphuric acid. The pale yellow plates and prisms are soluble in water and the aq. soln. has a mol. conductivity of 229·35, 250·0, and 266·72 for soln. with a mol in 100, 300, and 900 litres respectively. Hence P. C. Ray and N. Dhar infer that the salt ionizes, forming two $Na^{\cdot}$-ions and the complex ion $Hg(NO_2)''_4$. P. C. Ray also obtained crystals of dihydrated **sodium mercuric tetranitrite,** $2NaNO_2.Hg(NO_2)_2.2H_2O$, in a similar way to the heptanitrite, but A. Rosenheim and K. Oppenheim said that the salt is anhydrous. Hot water decomposes the salt with the separation of mercury and mercuric oxide. P. C. Ray obtained crystals of tetrahydrated **lithium mercuric hexanitrite,** $4LiNO_2.Hg(NO_2)_2.4H_2O$, by the process employed for potassium mercuric tetranitrite; and the mother-liquor gave crystals of hydrated **lithium mercuric trinitrite,** $LiNO_2.Hg(NO_2)_2.H_2O$. F. Ephraim prepared *potassium copper mercuric octochlorotetranitrite,* $K_2[Cu(NO_2)_4.H_2O]2K_2[HgCl_4.H_2O]$, in thick black prisms which may be a solid soln. or a mixture. P. C. Ray prepared **barium mercuric heptanitrite,** $2Ba(NO_2)_2.3Hg(NO_2)_2.5H_2O$, by evaporating under reduced press. over sulphuric acid, a soln. of the component salts. The dry salt is stable in a desiccator, but if not well dried, nitrous vapours may be given off. P. C. Ray and S. C. Mukherjee estimated the degree of ionization to be 3·34 for a dilution $v=126·0$ litres. P. C. Ray also made **strontium mercuric heptanitrite,** $2Sr(NO_2)_2.3Hg(NO_2)_2.5H_2O$, and **calcium mercuric heptanitrite,** $2Ca(NO_2)_2.3Hg(NO_2)_2.5H_2O$, in a similar manner. P. C. Ray and S. C. Mukkerjee estimated that for a dilution $v=42·1$ litres the degree of ionization for the calcium mercuric salt is 1·86.

P. C. Ray[8] has prepared **dimercuriammonium nitrite,** NHg_2NO_2, or, as E. C. Franklin prefers to represent it, $Hg:N.Hg.NO_2$, **mercuric mercuriimidonitrite.** According to P. C. Ray and A. C. Ghosh, when dried at 95°, it retains about half a mol of water. E. C. Franklin represented the composition of the *hemihydrate* by $HO.Hg.NH.Hg.NO_2.Hg_2N.NO_2$. K. A. Hofmann and E. C. Marburg, and E. C. Franklin prepared a *monohydrate* which the latter represents by the formula $HO.Hg.NH.HgNO_2$. P. C. Ray prepared this salt as follows: mercurous nitrite is acted on by water so as to obtain a soln. of mercuric mercurous nitrite, which is then changed to one of mercuric-sodium nitrite by careful addition of just enough sodium chloride. Another and better way of preparing mercuric-sodium nitrite soln. is to dissolve mercurous nitrite in a concentrated soln. of sodium nitrite, when half the mercury separates as metal. To the mercuric-sodium nitrite soln., filtered from the mercurous chloride dil. ammonia is gradually added until in slight excess. A cream-coloured, flocculent, but somewhat dense precipitate is produced, which is washed on a filter by aid of the suction-pump. Being slightly decomposed in the steam-oven, it has to be dried over sulphuric acid, and as it then collects into compact lumps, these are broken up and again exposed in the desiccator in order to facilitate the drying. The dry salt is pale yellow. When heated in a bulb-tube, the salt decomposes without fusing, giving off nitrous fumes, mercury, and water, and leaving a yellow residue—mostly mercuric oxide; and it gives most of its nitrogen as ammonia when heated with 20 per cent. potash-lye. P. C. Ray and A. C. Ghosh said that by analogy with the other dimercuric-ammonium salts, it might be anticipated that the nitrite would decompose: $2NHg_2NO_2=N_2+2Hg+2HgNO_2$, and that the mercurous nitrite so formed would yield its own products of decomposition. The temp. of decomposition is near 140°. Nitrous acid was found among the products of decomposition. They consider that the decomposition occurs in about four directions simultaneously: (i) $NHg_2NO_2=N_2+2HgO$; (ii) $NHg_2NO_2=N_2O+HgO+Hg$; (iii) $NHg_2NO_2=N_2+2Hg+O_2$; and (iv) $3NHg_2+3NO_2=Hg(NO_3)_2+2N_2+5Hg$. The nitrite can be converted into chloride, bromide, or nitrate.

The *nitrites of boron, aluminium, gallium, and indium* have not been reported.

F. Vogel[9] prepared **thallous nitrite,** $TlNO_2$, by mixing eq. proportions of aq. soln. of the component salts, and evaporating the filtrate on a water-bath. The yellow crystalline mass is soluble in water, but not in absolute alcohol. Crystals of the salt are precipitated from its aq. soln. by alcohol. The salt does not change in weight on heating at 140° ; but V. Thomas found that at a higher temp., it decomposes into thallous oxide and nitrogen oxide. W. C. Ball and H. H. Abram prepared thallium nitrite from a soln. of barium nitrite and thallous chloride. The evaporation of the liquid over sulphuric acid, or on a water-bath, furnishes a deep orange-red, crystalline mass. The salt readily fuses without decomposition; it is more soluble in water than the nitrate. L. Rolla and G. Belladen observed that thallous nitrite has a sp. conductivity below that of the nitrate, and undergoes normal ionization. The e.m.f. of the cell $Tl_{amalgam} \mid 0{\cdot}1N\text{-}TlNO_2$ with the normal electrode is 0·667 at 25°, and the same value is obtained if the nitrate be replaced by the nitrate. They obtained no complex salts with potassium nitrite and thallous nitrate. V. Cuttica found that the thermal behaviour of fused mixtures of thallium nitrite and nitrate excludes the formation of complexes. The two salts form an uninterrupted series of solid soln. V. Cuttica and A. Paciello observed that in aq. soln., thallous nitrite, like the alkali nitrites, is highly ionized, and the salt shows no tendency to form either complex or double nitrites; with cupric nitrate, thallous nitrite forms **thallous copper nitrite,** or *thallous cuprinitrite,* $Tl_3[Cu(NO_2)_5]$, in opaque, black, rounded crystals. This yields a pale green, aq. soln., and is decomposed by dil. acid, with formation of a blue soln. and liberation of nitrous acid. At the ordinary temp., both the solid salt and its aq. soln. are stable. In order to trace the displacement of the equilibria produced in soln. of cupri-nitrous complexes by variation of the relative conc. of the components, conductivity measurements have been made on soln. containing cupric chloride and barium nitrite in different proportions. The conductivity-composition curve shows two inflexions, due to the appearance of two complexes corresponding with the ions, $[Cu(NO_2)]$ and $[Cu(NO_2)_2]$. G. Canneri found that the treatment of a suspension of thallium sesquioxide in water with liquid nitrous anhydride, and subsequent evaporation of the soln., even in the cold under reduced press., yields, not thallic nitrite, but thallous nitrate. The latter is also obtained when soln. of thallic sulphate and barium nitrite are mixed in the cold, and the resulting liquid evaporated at low temp. That **thallic nitrite** is capable of existence in soln., although it cannot be obtained in the solid condition, is shown by the analyses and properties of the soln. The treatment of an aq. soln. of thallic nitrite with alcohol yields a precipitate of the sequioxide. In ethereal soln., thallic nitrite is far more stable, and the salt separates in the solid state on evaporation of the solvent; it could not, however, be analyzed directly. Decomposition of thallic nitrite, with formation of thallous nitrate, takes place solely in accordance with the equation $Tl(NO_2)_3 \rightarrow TlNO_3 + N_2O_3$, neither intermediate reduction products nor thallous-thallic complex compounds being formed. F. T. Frerichs and E. F. Smith obtained *didymium nitrite* in aq. soln. as a dark brown viscid liquid. G. Krüss and A. Loose attempted to prepare *yttrium and cerium nitrites* and to use the result as a means of separation of the earths. G. T. Morgan and E. Cahen obtained **cerous nitrite** contaminated with a small proportion of hydroxide by mixing eq. proportions of cold aq. soln. of cerous sulphate and barium nitrite. The pale yellow soln. was evaporated over potassium hydroxide in vacuo. The scum of basic nitrite was removed by filtration, and the yellow filtrate, when further concentrated, deposited yellow crystals. The salt is unstable, and evolves nitrous fumes at ordinary temp.; it is decomposed by warm water. The soln. yields basic nitrites when treated with alcohol. V. Cuttica and F. Gallo prepared the triple salt **ammonium copper cerous nitrite,** $15NH_4NO_2.4Cu(NO_2)_2.3Ce(NO_2)_3$, in black crystals which form a green soln. with water; **potassium copper cerous nitrite,** $12KNO_2.4Cu(NO_2)_2.Ce(NO_2)_3$, and **thallium copper cerous nitrite,** $5TlNO_2.3Cu(NO_2)_2.Ce(NO_2)_3$. H. Erdmann, and L. Pissarjewsky found that sodium and potassium nitrites precipitate thorium hydroxide from *thorium salts; titanium and zirconium salts* behave similarly.

No *tin nitrite* has been reported. J. L. Proust[10] prepared a lead nitrite by the action of metallic lead on a soln. of lead nitrate; and A. Thiel and L. Stoll showed that at 25° about 40 per cent. of the nitrate forms nitrite, and some basic nitrates as well. The reduction proceeds further at 100°, and in the presence of acetic acid. M. E. Chevreul, J. J. Berzelius, and E. Péligot prepared hydrated **lead nitrite,** $Pb(NO_2)_2.H_2O$, by passing a soln. of nitric oxide through a soln. of the basic nitrite in hot water; carbon dioxide was passed into the soln. to remove lead oxide, and the yellow filtrate was either evaporated spontaneously or under reduced press. J. Lang obtained it by double decomposition with a soln. of lead chloride and silver nitrite, and evaporating the clear soln. A. Chilesotti mixed theoretical proportions of soln. of lead chloride and lead nitrite, sat. at 25°; the soln. was cooled to —12° or —15° with vigorous stirring, and the clear filtrate evaporated to about one-sixth its bulk, and then allowed to stand in a desiccator over sulphuric acid. E. Müller and H. Barck made the normal nitrite by the action of nitric oxide on lead dioxide at ordinary temp., or on red-lead at 200°. P. Sabatier and J. B. Senderens passed nitric oxide into water in which lead dioxide was suspended. A. Thiel and L. Stoll found that by the action of lead on lead nitrate soln. at 25°, about 40 mol. per cent. of the nitrate undergoes reduction to nitrite, part of which separates together with nitrate as basic salts. This reduction is more complete at 100° or in the presence of acetic acid. Conversely, lead nitrite soln. alone, or in the presence of lead, partially changes to nitrate with the simultaneous separation of basic salts. The latter change makes the preparation of pure lead nitrite very difficult. The pure nitrite can, however, be obtained by treating solid silver nitrite with solid lead bromide in the presence of a small quantity of water. The yellow tabular or prismatic crystals are stable in air, but are easily decomposed. The salt readily dissolves in water, and the aq. soln. decomposes on evaporation. A. Chilesotti noticed that some nitrous fumes are evolved on evaporating the aq. soln. in vacuo at ordinary temp. The eq. conductivity, λ, for soln. with an eq. of salt in v litres is, at 20°:

v .	16	32	64	128	256	512	1024
λ .	59·4	72·3	85·5	98·9	111·3	122·1	129·7

The $0·1N$-soln. is less ionized than a corresponding soln. of lead nitrate, and about the same as one of lead chloride; conc. aq. soln. are worse conductors than those of lead nitrate or chloride. The conductivity increases with time, probably owing to a reaction: $3Pb(NO_2)_2+2H_2O=Pb(NO_3)_2+2Pb(OH)_2+4NO$. In the absence of air, lead nitrate and hydroxide are formed, the soln. becomes alkaline, and nitric oxide mixed with a little hydrogen is evolved. At 100°, equilibrium occurs when about 13 per cent. of the nitrite is transformed. If air be present, the decomposition goes further. According to A. Chilesotti, if a soln. of 25 grms. of lead nitrate in 1·5 litres of water is boiled for 5 hrs. along with 31 grms. of lead, an orange-yellow precipitate of **lead dioxynitrite,** $2PbO.Pb(NO_2)_2$, is produced, and F. Peters, and C. Bromeis obtained a similar product by boiling the orange-yellow basic nitritonitrate; and F. Peters, from the filtrate obtained in preparing some of the basic nitritonitrates. N. von Lorenz, and F. Peters said that the salt forms rhombic prisms which occur as masses or concentric tufts of needle-like crystals.

A number of other basic nitrites have been reported, but there is no proof of the individuality of these basic salts. P. Sabatier and J. B. Senderens made the same salt from the soln. obtained in their process of making normal lead nitrite; and R. Weinland and F. Paul, by the action of a soln. of sodium nitrite on a boiling soln. of lead oxychlorate. Thus, J. J. Berzelius, M. E. Chevreul, N. von Lorenz, E. Péligot, A. Chilesotti, and F. Peters described $4PbO.N_2O_3.H_2O$, or *lead trioxydinitrite,* $3PbO.Pb(NO_2)_2.H_2O$, or $2PbO.Pb(OH)_2.Pb(NO_2)_2$, as a red powder. F. Peters made yellowish-brown crystals of $10PbO.3N_2O_3.H_2O$, or *lead heptoxyhexanitrite,* $7PbO·3Pb(NO_2)_2.H_2O$, or $6PbO.Pb(OH)_2.3Pb(NO_2)_2$, and yellowish-green crystals of $7PbO·3Pb(NO_2)_2.3H_2O$, or $4PbO.3Pb(OH)_2.3Pb(NO_2)_2$;

A. Chilesotti, *lead dioxydinitrite*, $2PbO.Pb(NO_2)_2.H_2O$, or $PbO.Pb(OH_2.Pb(NO_2)_2$; N. von Lorenz, crystals of *lead henicosoxydocosinitrite*, $21PbO.11Pb(NO_2)_2.H_2O$, or $20PbO.Pb(OH)_2.11Pb(NO_2)_2$; and C. Bromeis, and A. Chilesotti, *lead oxydinitrite*, $PbO.Pb(NO_2)_2.H_2O$, or $Pb(OH)_2.Pb(NO_2)_2$, and the same salt with an addition 0·5 or 1 mol H_2O.

J. J. Berzelius obtained normal **lead hexanitritodinitrate,** $3Pb(NO_2)_2.Pb(NO_3)_2.4H_2O$, by adding enough sulphuric acid to a soln. of $2Pb(OH)_2.Pb(NO_2)_2.Pb(NO_3)_2$ to precipitate half the lead, or by passing carbon dioxide through the soln. so long as lead carbonate is precipitated. Lemon-yellow octahedra are obtained by evaporation in vacuo. M. E. Chevreul also prepared this salt, and observed that a crop of white needles appeared before the yellow octahedra. J. J. Berzelius, M. E. Chevreul, J. Nicklès, and A. Gomes regarded the salt as a chemical individual; E. Péligot, and A. Chilesotti, as a mixture.

A. Stromeyer observed the formation of a yellow precipitate when an acetic acid soln. of a lead salt is treated with potassium nitrite. N. W. Fischer, and W. Hampe prepared **potassium lead heptanitrite,** $K_3Pb_2(NO_2)_7.(0 \text{ to})1{\cdot}5H_2O$, by evaporating a mixed soln. of lead nitrite or acetate and potassium nitrite; needle-like crystals separate from the soln. in hot water; A. Chilesotti obtained it by mixing hot conc. soln. of 2 mols of potassium nitrite and one of lead acetate, and washing the precipitate with alcohol; and it crystallizes from a soln. of lead acetate and an excess of potassium nitrite. The orange-yellow, six-sided, monoclinic needles or prisms are stable in air. W. Hampe found them to be readily soluble in water, and less soluble in alcohol. J. Lang prepared **potassium lead tetranitrite,** $K_2Pb(NO_2)_4.H_2O$, by evaporating a soln. of lead acetate and an excess of potassium nitrite; and by the action of an excess of potassium nitrite on a soln. of lead nitrate. A. Chilesotti also prepared the salt. It furnishes orange-yellow prisms, which are readily soluble in water, but not in alcohol. The aq. soln. reacts neutral; there is a slight hydrolysis when the aq. soln. is evaporated; aq. ammonia and potassium carbonate give white precipitates with a soln. of the salt.

A. Chilesotti obtained a basic salt, **potassium lead oxypentanitrite,** $KNO_2.PbO.2Pb(NO_2)_2$, by treating a soln. of the tetranitrite with lead hydroxide, or by evaporating an aq. soln. of the tetranitrate. S. D. Hayes reported **potassium lead dinitritodinitrate,** $2KNO_3.Pb(NO_2).H_2O$, by passing nitric oxide into a supersaturated soln. of lead nitrate in potash-lye. A. N. Meldrum represented its composition $K_2Pb(NO_2)_3(NO_3).H_2O$. J. Lang, and F. Peters reported orange-yellow prisms of **potassium lead octonitritotetranitrate,** $K_6Pb_3(NO_2)_8(NO_3)_4.3H_2O$.

C. Przibylla prepared the triple salt **ammonium copper lead nitrite,** $CuPb(NH_4)_2(NO_2)_6$, by adding a soln. of copper and lead nitrites to a soln. of ammonium nitrite and sodium nitrite. The product is a black, crystalline salt having a bluish, metallic lustre; it is stable at the ordinary temp. or when gently warmed, and is very similar to the corresponding potassium salt. Like this salt, all the other triple nitrites contain $6NO_2$. A. H. van Lessen reported **potassium copper lead hexanitrite,** $K_2CuPb(NO_2)_6$, or, according to F. Ephraim, $K_2Pb[Cu(NO_2)_6]$, to be precipitated by adding acetic acid to a mixed soln. of cupric nitrate, lead acetate, and potassium nitrite. The dark green cubic crystals have a sp. gr. 3·345 at 15°.

F. von Oefele[11] found that when nitric acid acts on tellurium, using large quantities of material and a high column of liquid (not less than 50 cms.), **tellurium nitrite** was obtained as a flesh-coloured precipitate, which could be dried at 100° without decomposition. At higher temperatures it decomposes, leaving a residue of yellow tellurium dioxide. O. T. Christensen[12] prepared a series of **chromic nitritopentammines,** $[Cr(NO_2)(NH_3)_5]X_2$, or *chromic xantho-salts*. For instance, **chromic nitritopentamminochloride,** $[Cr(NO_2)(NH_3)_5]Cl_2$, was obtained as follows:

Twenty grams of chromic chloropentamminochloride are treated with 300 c.c. of water and a few drops of nitric acid, and the soln. is heated until all is dissolved. It is then left at rest, and should any unaltered chromic chloropentamminochloride separate out, it is filtered off and treated as before. To the soln. of chromic aquopentamminochloride obtained in this way 40 to 50 grms. of sodium nitrite and 25 c.c. of dil. hydrochloric acid are added, and the mixture stirred, when a yellow crystalline precipitate of chromic nitritopentamminochloride separates out; this is collected, washed with water and with alcohol, and dried at the ordinary temp. In order to purify it, the chloride is dissolved in water and filtered into a soln. of ammonium chloride; the precipitated chromic nitritopentamminochloride is collected, washed with water to remove ammonium chloride, then with alcohol, and dried at the ordinary temp.

Chromic nitritopentamminochloride is a yellow crystalline powder composed of microscopic octahedra; it is more soluble in water than chromic chloropentamminochloride, and less soluble than chromic aquopentamminochloride. According to A. Werner and A. Miolati, the mol. conductivity of soln. with a mol of the salt in v litres of water at 25°, is:

v	125	250	500	1000	2000
μ	221·0	239·3	252·0	261·0	271·6

O. T. Christensen observed that the aq. soln. of the nitritopentamminochloride in acids liberate nitrous acid from it, and hydrochloric acid converts it into chromic chloropentamminochloride. Sodium hydroxide dissolves it, forming a soln. which probably contains *chromic nitritopentamminohydroxide*, and from which chromic hydroxide separates on boiling; ammonia is also evolved. Aq. ammonia has no action on chromic nitritopentamminochloride. Cold aq. soln. of chromic nitritopentamminochloride give the following reactions: (1) With platinum chloride, a yellow crystalline precipitate consisting of needles or prismatic crystals. (2) With hydrogen fluosilicate, no precipitate, but the salt is decomposed. (3) With the double chloride of sodium and mercury, a yellowish-red crystalline precipitate. (4) No precipitates with ferro- or ferri-cyanide of potassium. (5) With potassium chromate and dichromate, beautiful yellow precipitates. (6) With sodium dithionate, a yellow crystalline precipitate, consisting of microscopic needles. Reaction is very characteristic for nitritopentamminochloride compounds. (7) With potassium and ammonium chlorides, potassium bromide, iodide, and nitrate, precipitates are obtained of the chloride, bromide, iodide, and nitrate respectively. Chromic nitritopentamminochloride furnishes a complex salt with mercuric chloride, $[Cr(NO_2)(NH_3)_5]Cl_2.2HgCl_2$, and the nitritopentammine forms a *bromide*, *iodide*, *nitrate*, a monohydrated *sulphate*, a monohydrated *dithionate*, *carbonate*, *chromate*, *dichromate*, and a *chloroplatinate*.

Normal **bismuth nitrite**, $Bi(NO_2)_3$, is unknown. L. Vanino and F. Hartl[13] prepared **bismuthyl nitrite**, $BiO(NO_2).\frac{1}{2}H_2O$, by adding sodium nitrite to an aq. soln. of mannitol bismuth nitrate. The yellowish-white precipitate decomposes above 60°, and readily dissolves in hydrochloric acid, forming a clear soln. on dilution.

W. C. Ball prepared **potassium hexanitritobismuthite**, or *potassium bismuth nitrite*, $K_3Bi(NO_2)_6.H_2O$, in orange- or golden-yellow plates, by precipitation on mixing conc. soln. of bismuth and potassium nitrites, with exclusion of air as far as practicable. The salt cannot be kept without decomposition more than a few days. W. C. Ball and H. H. Abram prepared **rubidium hexanitritobismuthite**, or *potassium bismuth nitrite*, $Rb_3Bi(NO_2)_6.2H_2O$, in a similar manner. The orange-yellow plates are less stable and less soluble than those of the potassium salt. Under similar conditions, **cæsium enneanitritodibismuthite**, or *cæsium bismuth nitrite*, $Cs_3Bi(NO_2)_6.Bi(NO_2)_3$, or $Cs_3Bi_2(NO_2)_9$, appears in place of the hexanitritobismuthite. The golden or orange hexagonal plates look like lead iodide. Under similar conditions **thallous heptanitritobismuthite**, or *thallous bismuth nitrite*, $Tl_3Bi(NO_2)_6.TlNO_2.H_2O$, is formed. The cæsium salt is the most electropositive, and it needs an extra molecule of bismuth nitrite, while the thallium salt is the most electronegative, and it needs an extra molecule of thallous nitrite.

W. C. Ball and H. H. Abram prepared a series of mixed salts of lithium nitritobismuthite. Thus, if 5 grms. of ammonium nitrate in 10 c.c. of water are added to a mixture of 16 c.c. of a 90 per cent. soln. of lithium nitrite and 4 c.c. of bismuth nitrate, cooled to 0°, a yellow crystalline precipitate of ammonium lithium hexanitritobismuthite, $(NH_4)_2LiBi(NO_2)_6.H_2O$, is formed; it decomposes when kept a few days, and it is hydrolyzed by water; yellow, octahedral crystals of potassium lithium hexanitritobismuthite, $K_2LiBi(NO_2)_6$, are produced in a similar way. The salt is quite stable, its sp. gr. is 3·21 at 15°, and it is easily hydrolyzed by water; similarly with rubidium lithium hexanitritobismuthite, $Rb_2LiBi(NO_2)_6$, which forms stable, yellow, octahedral crystals less soluble than the potassium salt; with cæsium lithium hexanitritobismuthite, $Cs_2LiBi(NO_2)_6$, in stable, yellow crystals less soluble than the rubidium salt; and with thallous lithium hexanitritobismuthite, $Tl_2LiBi(NO_2)_6$, in stable, pale brown, probably octahedral crystals sparingly soluble in water. By adding a soln. of silver nitrate to a soln. of ammonium nitrite containing bismuth nitrate, or better, by adding to an aq. soln. of sodium nitrite first bismuth nitrate and then silver nitrate, and treating the liquid with ammonium nitrate, a red crystalline precipitate of ammonium silver hexanitritobismuthite, $(NH_4)_2AgBi(NO_2)_6$, is formed. The salt is soluble in water; is hydrolyzed by water; is fairly stable at ordinary temp.; but when dry explodes feebly when rubbed in a mortar. W. C. Ball and H. H. Abram also prepared potassium silver hexanitritobismuthite, $K_2AgBi(NO_2)_6$, in orange-red, octahedral crystals less soluble than the ammonium salt; rubidium silver hexanitritobismuthite, $Rb_2AgBi(NO_2)_6$, in stable orange-yellow, probably octahedral crystals, which are sparingly soluble, and hydrolyzed by water; cæsium silver hexanitritobismuthite, $Cs_2AgBi(NO_2)_6$, in pale yellow, sparingly soluble crystals, slowly decomposed by water; blackened in light; but stable in darkness; and thallous silver hexanitritobismuthite, $Tl_2AgBi(NO_2)_6$, as a stable, red crystalline powder, very sparingly soluble in water, and slowly hydrolyzed by that menstruum. A stable yellow **ammonium sodium hexanitritobismuthite,** $Bi(NO_2)_3.2(NH_4)NO_2.NaNO_2$, or $(NH_4)_2NaBi(NO_2)_6$, crystallizing in octahedra, is obtained by dissolving bismuth nitrate in a conc. soln. of ammonium nitrate, and adding the resulting liquid to a sat. soln. of sodium nitrite at 0°, and acidified with nitrous fumes; similarly with potassium sodium hexanitritobismuthite, $K_2NaBi(NO_2)_6$, an unstable yellow, crystalline powder, which is hydrolyzed by water; rubidium sodium hexanitritobismuthite, $Rb_2NaBi(NO_2)_6$, as a yellow crystalline powder; cæsium sodium hexanitritobismuthite, $Cs_2NaBi(NO_2)_6$, and thallous sodium hexanitritobismuthite, $Tl_2NaBi(NO_2)_6$, in large, honey-yellow crystals which are fairly stable and slowly decomposed at 100°. The *monohydrate* was also prepared. W. C. Ball reported an unstable, yellow salt, probably **ammonium sodium bismuth nitratonitrite,** $Bi(NO_2)_3.2(NH_4)NO_2.(NH_4)NO_3.NaNO_3$, to be precipitated by dissolving bismuth nitrate in a soln. of sodium nitrite, and pouring the resulting orange-coloured liquor into a sat. soln. of ammonium nitrate at 0°. For complexes with nickel, *vide infra.* F. Ephraim prepared **cæsium copper lead hexanitrite,** $Cs_2Pb[Cu(NO_2)_6]$, in black, microscopic crystals, sparingly soluble in water. L. Rolla and G. Belladen obtained some complex salts from soln. of lead nitrate and thallous nitrite; and V. Cuttica and A. Paciello prepared **thallous lead nitrite,** $Tl_2Pb(NO_2)_4.H_2O$, from soln. of lead acetate and thallous nitrite, evaporated in vacuo. The orange-red crystals are more stable than lead nitrite, and the aq. soln. on heating separates lead hydroxide.

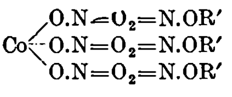
J. A. Arfvedson[14] said that **uranyl nitrite** is formed when uranyl nitrate, $UO_2(NO_3)_2.6H_2O$, is heated; at a dull red heat, uranosic oxide is formed. The work of W. O. de Coninck makes this statement somewhat doubtful.

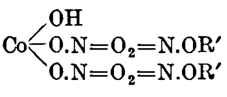
According to C. J. B. Karsten,[15] when small quantities of hydrated manganic dioxide are treated with nitric oxide in the presence of water, **manganous nitrite,** $Mn(NO_2)_2$, is formed; while with large quantities, manganous nitrate is formed. E. Mitscherlich, and J. Lang showed that when an attempt is made to concentrate the soln., hydrolysis occurs, and hydrated manganese dioxide is precipitated. Neither **ferrous nitrite** nor **ferric nitrite** has been prepared; but C. Przibylla obtained some triple salts. Thus, a bright yellow precipitate which is apparently a mixture of salts is obtained on mixing equivalent quantities of ferrous chloride, barium chloride, and potassium chloride with the necessary quantity of sodium nitrite; by varying the proportions of the metallic salts, various mixtures of salts are obtained. A compound of the formula $FeBaK_2(NO_2)_6$, **potassium barium iron nitrite,** is obtained by mixing a soln. of ferrous chloride, [12·5 c.c. (1 c.c.=0·1943 grm. Fe)], potassium chloride (13 grms.), and crystallized barium chloride (22 grms.) in 120 c.c. of water with 100 c.c. of a soln. of sodium nitrite (10 c.c.=5 grms. sodium nitrite); the precipitate is quickly separated by filtration, washed with alcohol, and dried at a gentle heat. Yellow to reddish-yellow precipitates of **potassium strontium nitrite**, and **potassium calcium nitrite** containing the three nitrites, are obtained in a similar manner to the above salts; but they contain varying proportions of each nitrite according to the relative amounts of the constituents employed. The author was unable to obtain a compound to which a simple formula could be assigned. The corresponding ammonium salts of iron nitrite can be obtained in a similar manner by employing small quantities of the constituents for each experiment; they are very similar to the potassium salts. **Iron lead potassium nitrite** is obtained on adding a soln. of ferrous and lead nitrates to a soln. of potassium nitrate and sodium nitrite as a heavy, reddish-yellow precipitate; this, after being washed by decantation with water, and then on a filter with alcohol, is an intense orange-yellow powder, insoluble in cold water and stable at the ordinary temperature.

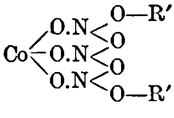
J. Lang,[16] W. Hampe, and C. F. Rammelsberg obtained a dark brown or a dark red soln. by mixing a soln. of barium nitrite and cobalt sulphate; it is thought that *cobaltous nitrite* is present; when the soln. is evaporated, some nitric oxide is given off. W. Hampe considered the red solid product is **cobaltosic nitrite.** W. R. E. Hodgkinson and N. E. B. Bellairs said that aq. ammonia exposed to air dissolves metallic cobalt, forming a nitrite; and C. Matignon and G. Desplantes observed that the metal is oxidized under these conditions. C. Duval obtained cobalt nitrite by the action of sodium or potassium nitrite, in the presence of ammonium acetate, on cobalt acetate, using ammonia, alcohol, or acetone as solvents. It is yellow and slightly soluble in water. During the evaporation of the reddish-brown soln. of cobaltous nitrite, some small dark brown crystals which formed were considered by J. Lang to be *cobaltic nitrite,* and by W. Hampe, basic cobaltic nitrite. According to A. Rosenheim and I. Koppel, when nitrous acid is added to a suspension of cobalt carbonate in water, a brown soln. is formed from which, on evaporation at ordinary temp., dark brown crystals of cobaltous nitrite are obtained along with crystals of **cobaltosic oxyhexanitritodinitrite,** $2CoO.2Co(NO_2)_3.Co(NO_3)_2.14H_2O$. There is therefore no satisfactory evidence that moderately pure cobaltous or cobaltic nitrite has been isolated. L. le Boucher treated a soln. of cobalt nitrate in pyridine and water with sodium nitrite at 0°; in an atm. of hydrogen, a light red **cobaltous tripyridinonitrite,** $Co(NO_2)_2.3C_5H_5N$, was obtained. By crystallization from pyridine, dark red crystals of **cobaltous hexapyridinonitrite,** $Co(NO_2)_2.6C_5H_5N$, were obtained. Both compounds were hydrolyzed by water. The latter compound was readily oxidized in air, mixed crystals of the nitrate being formed.

O. L. Erdmann reported **potassium cobaltous tetranitrite,** $K_2Co(NO_2)_4$, or $6KOH.3Co_3(NO_2)_2$, to be separated as a yellow crystalline powder when soln. of cobaltous chloride and an excess of potassium nitrite are mixed. No oxygen is absorbed from the air during its formation, and O. L. Erdmann, and S. P. Sadtler used an atm. of carbon dioxide. The salt was also prepared by A. Stromeyer, and C. D. Braun. The salt is insoluble in cold water, but soluble in hot water, forming a red soln. It forms a violet soln. if potassium acetate is present, containing cobaltous salts. The salt decomposes when heated. C. D. Braun said that cobaltic hydroxide is precipitated when the soln. is boiled with potash-lye. O. L. Erdmann said that the cobalt is not contained in the salts as a base in the ordinary sense of the word. C. D. Braun supposed that the cobalt is present as sesquioxide. C. W. Blomstrand has discussed the constitution of the salt. For **potassium cobalt diamminotetranitrite,** $K[Co(NH_3)_2(NO_2)_4]$, *vide infra.* S. P. Sadtler obtained black or dark green cubic crystals of $KCo(NO_2)_2.\frac{1}{2}H_2O$, **potassium cobaltous dinitrite,** by mixing a dil. soln. of potassium nitrite and a hot soln. of cobaltous chloride; and the mother-liquid furnishes a yellow flocculent precipitate of **potassium cobaltous trinitrite,** $K_2Co(NO_2)_2.H_2O$. The same salt was made by mixing hot conc. soln. of potassium nitrite and cobaltous chloride. A. Rosenheim and I. Koppel made **potassium cobaltic oxyoctonitrite,** $Na_4Co_2(NO_2)_8O$, by the method indicated below for the sodium salt.

According to G. C. Williamson and P. Berckman, *aureolin*, or *cobalt yellow*—a double nitrite of cobalt and potassium—was first used as a pigment about 1800, and possibly a little earlier. N. W. Fischer made **potassium cobaltic nitrite,** $K_3Co(NO_2)_6.1\frac{1}{2}H_2O$, as a yellow powder, by mixing an acidified soln. of cobaltous chloride with potassium nitrite. E. St. Evre, and A. Stromeyer prepared the salt in a somewhat similar way; and the former also treated with an excess of potassium nitrite the blue precipitate obtained by adding potassium hydroxide to cobaltous nitrate; the same salt was obtained by treating the precipitate and mother-liquor with nitric oxide. A. Rosenheim and I. Koppel made the salt by suspending freshly precipitated cobaltous chloride in a small proportion of water, adding the calculated quantity of potassium hydroxide, carbonate, or nitrite, and then mixing the mass with nitrous acid until the cobalt carbonate is all dissolved. The analyses of the salt—by O. L. Erdmann, C. D. Braun, S. P. Sadtler, M. Cunningham and F. M. Perkin, A. Stromeyer, and E. St. Evre—are not very concordant. C. W. Blomstrand, and A. Rosenheim and I. Koppel discussed the constitution of the salt. While A. Werner represented the constitution of the three series of complex cobaltic nitrites by $[Co(NO_2)_6]M'_3$; $[Co(NO_2)_4X]_3M'$; and $[Co(NO_2)_3X_3]$, A. Rosenheim and I. Koppel represented them graphically as derivatives of orthonitrous acid, $N(OH)_3$:







The yellow crystals consist of four-sided prisms. C. D. Braun found that the salt, dried at 40°–60°, does not change in weight at 100°, but at 200° it loses about 23·73 per cent. in weight. According to E. St. Evre, when the salt is heated in a sealed tube, it becomes orange-yellow, and melts, giving off water, nitrogen peroxide, and nitrous acid, and leaves behind a mixture of cobalt sesquioxide and potassium nitrite. If heated in dry carbon dioxide, nitric oxide and nitrogen are also formed; in hydrogen, acid vapours, and ammonia are produced; the residue, with water, yields cobalt, and an alkaline liquid containing some cobalt. The salt potassium cobaltic hexanitrite is sparingly soluble in cold water; T. Rosenbladt said that at 17°, 1000 parts of cold water dissolve 0·893 part of salt. The salt is decomposed by hot water with the exclusion of air, forming nitric oxide; if air be present, nitric fumes are evolved and the liquid becomes alkaline and rose-red, forming ordinary cobaltous and potassium nitrites. A. Rosenheim and I. Koppel said that when boiled with water, the salt dissolves with the evolution of nitric acid, and the evaporation of the soln. furnishes a mixture of red and yellowish-brown crystals which cannot be separated. E. St. Evre said that the salt is not soluble in alcohol or ether, and only a trace dissolves in carbon disulphide. M. Pierrat found that with soln. containing the following percentage amounts of alcohol, the solubilities, in grams per litre, were:

Alcohol . .	94·7	42·4	27·3	15·9	8·7	0 per cent.
Solubility . .	0·026	0·033	0·036	0·056	0·09	0·21

A. Stromeyer found it to be insoluble in cold or hot of fairly concentrated soln.

of potassium sulphate, chloride, nitrate, or acetate; but in a soln. of sodium or ammonium chloride it is more soluble than it is in water. E. St. Evre found that chlorine does not decompose the salt in the cold, nor does cold hydrochloric or nitric acid dissolve the salt, but when heated the salt is decomposed with the evolution of red vapours. Hydrogen sulphide attacks the salt suspended in water, very slowly; but ammonium sulphide very quickly forms a black sulphide. According to C. D. Braun, a boiling soln. of sodium hydrophosphate decomposes the salt with the separation of a blue precipitate, and the filtrate contains nitric acid. A boiling conc. soln. of sodium pyrophosphate furnishes a clear brownish olive-green liquid which becomes paler when boiled; when the cold liquid is treated with potassium cyanide, and a little acetic acid, potassium cobaltinitrocyanide, $K_4Co_2Cy_9(NO_2).3H_2O$, is formed. According to A. Stromeyer, potassium hydroxide acts on the salt with difficulty, and, added C. D. Braun, and R. Wegscheider, if a conc. soln. is employed, the salt becomes greenish-yellow. A. Stromeyer showed that hot soda-lye, or hot baryta-water, decomposes the salt, forming brown cobaltic hydroxide if air be absent. C. D. Braun found that hot lime-water acts similarly. If the salt be boiled with water and silver carbonate, cobaltic hydroxide is precipitated and the liquid on evaporation yields colourless needles which S. P. Sadtler considered to be silver nitrite. Further, a boiling soln. of ferrous sulphate results in the separation of ferric hydroxide and the formation of nitrous acid. The salt is not decomposed by potassium cyanide, but, added A. Rosenheim and I. Koppel, a conc. soln. of potassium cyanide heated on a water-bath decomposes much of the salt with the evolution of nitrogen and nitrous oxide, forming a brown soln. which contains potassium cobalticyanide. For the cobaltic amminonitrite, *vide infra.*

A. Rosenheim and I. Koppel prepared yellow **rubidium cobaltic hexanitrite,** $Rb_3Co(NO_2)_6$, by the method for the potassium salt. T. Rosenbladt obtained it by boiling a soln. of equal parts of cobaltous nitrate and sodium acetate in 15 parts of water, adding 20 per cent. acetic acid, and stirring up the mixture with a conc. soln. of sodium nitrite. T. Rosenbladt said that 1000 parts of water at 17° dissolve 0·0505 part of the salt. Hence, H. Erdmann said that it is the least soluble of all the rubidium salts. T. Rosenbladt, and H. Erdmann also prepared yellow **cæsium cobaltic hexanitrite,** $Cs_3Co(NO_2)_6$. According to the former, 1000 parts of water at 17° dissolve 0·0497 part of the salt. According to A. Stromeyer, sodium nitrite gives no precipitate with a soln. of cobaltous chloride and sodium acetate. C. D. Braun obtained no complex salt by treating soln. of cobaltous salts with sodium hydroxide and nitrite.

A. Rosenheim and I. Koppel found that if an excess of a conc. soln. of sodium nitrite be added to a boiling soln. of cobaltous chloride and acetic acid, some nitric oxide is evolved, and a yellow salt, $Na_2Co(NO_2)_5.\frac{1}{2}H_2O$, sodium cobaltic pentanitrite, is precipitated. S. P. Sadtler washed the salt with a soln. of sodium acetate, and then with alcohol. A. Rosenheim and I. Koppel also prepared a basic salt, $Na_4Co_2(NO_2)_8O$, **sodium cobaltic oxyoctonitrite,** by allowing the brown mother-liquors obtained in the preparation of the hexanitrite to evaporate over sulphuric acid; a reddish-brown, crystalline powder is obtained, which is not, however, the pure salt; when dissolved in water, it is not precipitated by alcohol; with nitrous acid, it yields the preceding salt; with potassium chloride, it does not give a precipitate, and when the mixture is allowed to evaporate over sulphuric acid, the corresponding potassium salt is obtained as a brown, microcrystalline powder. S. P. Sadtler, and M. Cunningham and F. M. Perkin prepared **sodium cobaltic hexanitrite,** $Na_3Co(NO_2)_6$, and A. Rosenheim and I. Koppel obtained it by the method employed for the potassium salt, but in this case, the salt is precipitated by adding alcohol to the black, filtered soln. The yellow precipitate was washed by suction with alcohol, and ether, and dried in air. A little of the oxyoctonitrite is present as impurity. The salt dissolves in water, forming a yellowish-brown soln. which gives off nitric oxide when heated. R. Wegscheider said that sodium cobaltic hexanitrite can be prepared readily by adding to a hot conc. soln. of sodium nitrite a soln. of a cobaltous salt, free from nickel, acidifying with acetic acid, and boiling for a few minutes. The soln. gives a yellow precipitate of potassium cobaltinitrite with potassium salts, is not precipitated by dil. sodium hydroxide soln. in the cold (indicating the absence of Co'' and $Co^{\cdot\cdot\cdot\cdot}$ ions), but yields a precipitate of cobaltic hydroxide on boiling, which shows that the complex salt contains tervalent cobalt and is decomposed by boiling alkalies. Alkaline soln. are not stable in the cold. The general reactions resemble those of the potassium salt, excepting the greater solubility of the sodium salt. N. Schiloff and B. Nekrassoff studied the adsorption of the salt by activated charcoal. R. H. Adie and T. B. Wood described **sodium dipotassium cobaltic nitrite,** $K_2NaCo(NO_2)_6.H_2O$, obtained as a yellow precipitate by adding the sodium salt to a one per cent. soln. of potassium chloride acidified with acetic acid. It does not lose its water of crystallization at 130°. Its solubility in water is rather less than one part in 20,000 parts. This salt was also obtained by W. A. Drushel, L. T. Bowser, and O. M. Shedd. W. C. Bray said that the precipitation is delicate enough to detect sixty parts of potassium per million. F. E. Brown and J. E. Snyder found that a crystal of this salt swells and blackens when boiled with vanadium oxytrichloride. L. L. Burgess and O. Kamm showed that the corresponding **disodium potassium cobaltic nitrite,** $NaK_2Co(NO_2)_6$, can also be made. **Lithium cobaltic hexanitrite,** $Li_3Co(NO_2)_6$, and **ammonium cobaltic hexanitrite,** $(NH_4)_3Co(NO_2)_6.1\frac{1}{2}H_2O$, were prepared by O. W. Gibbs and T. A. Genth, O. L. Erdmann, S. P. Sadtler, W. C. Ball and H. H. Abram, and A. Rosenheim and I. Koppel.

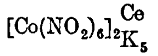
A. Rosenheim and I. Koppel obtained a green compound, thought to be **copper cobaltic nitrite,** by the action of sodium cobaltic nitrite on a cupric salt. M. Cunningham and F. M. Perkin prepared **silver cobaltic hexanitrite,** $Ag_3Co(NO_2)_6$, as an orange-yellow salt, fairly soluble in water, by adding a soln. of silver nitrate to a conc. soln. of sodium cobaltic nitrite. L. L. Burgess and O. Kamm also obtained the intermediate salts **potassium disilver cobaltic hexanitrite,** $Ag_2KCo(NO_2)_6$, and **dipotassium silver cobaltic hexanitrite,** $K_2AgCo(NO_2)_6$. They also obtained **rubidium silver cobaltic hexanitrites, cæsium silver cobaltic hexanitrites, thallium silver cobaltic hexanitrites,** and **ammonium silver cobaltic hexanitrites.** A. Rosenheim and I. Koppel also reported **silver cobaltic oxyhexanitrite,** $2Ag_2O.Co_2O_3.3N_2O_3.3H_2O$, to be formed when silver nitrate is treated with a soln. of the potassium salt. It is sparingly soluble in water, and is decomposed by boiling water with the formation of silver nitrite. A. Rosenheim and I. Koppel prepared **barium cobaltic dodecanitrite,** $Ba_3Co_2(NO_2)_{12}.14H_2O$, from a soln. of sodium cobaltic hexanitrite and barium chloride; or by the action of nitrous acid on cobalt carbonate and barium nitrite suspended in water. The deep brown soln. is filtered before all the cobalt carbonate is dissolved, and then treated with more nitrous acid. The conc. soln. gives a yellow or brownish-yellow microcrystalline powder; the crystals are six-sided plates. The salt is less stable than the corresponding alkali salts. It is almost insoluble in cold water, and is decomposed by hot water. The corresponding **strontium cobaltic dodecanitrite,** and **calcium cobaltic dodecanitrite** were not analyzed. The mother-liquor from barium cobaltic dodecanitrite, containing a slight excess of cobalt carbonate when evaporated over sulphuric acid, furnishes a crop of crystals of the dodecanitrite and afterwards dark red crystals of **barium cobaltic oxyoctonitrite,** $Ba_2Co_2O(NO_2)_8$, which dissolve in warm water without decomposition. Corresponding **strontium cobaltic oxyoctonitrite,** $Sr_2Co_2O(NO_2)_8$, and **calcium cobaltic oxyoctonitrite** were also prepared. **Magnesium cobaltic hexanitrite,** $Mg_3[Co(NO_2)_6]_2$, has also been made. Dark red crystals of **zinc cobaltic oxytrinitrite,** $ZnCoO(NO_2)_3$, were also prepared. S. C. Ogburn prepared **cadmium cobaltic dodecanitrite,** $Cd_3[Co(NO_2)_6]_2$, by double decomposition with sodium cobaltic nitrite and a sat. soln. of cadmium sulphate. The product was isolated from the mother-liquor by fractional crystallization. It is canary-yellow in colour, and stable both in soln. and in the solid form. It is slightly hygroscopic; insoluble in cold water, but readily soluble in boiling water; and slightly soluble in alcohol or ether. He also prepared three bismuth salts: **bismuthyl cobaltic tetranitrite,** $(BiO)_3Co(NO_2)_4$; **bismuthyl cobaltic pentanitrite,** $(BiO)_3Co(NO_2)_5$, and **bismuthyl cobaltic hexanitrite,** $(BiO)_3Co(NO_2)_6$. The first-named salt is the most stable. The colours range from yellow to orange; they are sparingly soluble in alcohol, and insoluble in ether. They are rapidly decomposed in soln. or in the solid state. They are produced by the action of sodium cobaltic nitrite on a sat. soln. of bismuth nitrate, and were obtained from the mother-liquor by rapid filtration at various stages of the precipitations. A. Rosenheim and I. Koppel prepared a **mercurous cobaltic hexanitrite,** $Hg_3Co(NO_2)_6$, by the action of a soln. of a mercurous salt on one of sodium cobaltic nitrite, and L. L. Burgess and O. Kamm said that it is the least soluble of all these complex cobaltic nitrites. S. M. Jörgensen, T. Rosenbladt, and M. Cunningham and F. M. Perkin prepared **thallium cobaltic hexanitrite,** $Tl_3Co(NO_3)_6$, as a scarlet-red salt by mixing soln. of thallous carbonate and of sodium cobaltic nitrite. T. Rosenbladt said that 1000 parts of water at 17° dissolve 0·0420 part of the salt. A. Rosenheim and I. Koppel obtained cubic crystals of **lead cobaltic dodecanitrite,** $Pb_3Co_2(NO_2)_{12}.12H_2O$, by a process like that used for the analogous barium salt. The product is stable when dry; it is almost insoluble in water; but decomposed, when suspended in water, by the passage of hydrogen sulphide. M. Cunningham and F. M. Perkin prepared the salt, but with $11H_2O$ not $12H_2O$. The complex amines—$Pb[Co(NH_3)_2(NO_2)_4]_2$, and $[Co_2(N_2O_2)(NH_3)_{10}]NO_3.\frac{1}{2}Pb(NO_3)_2$—are described below. A. Stromeyer reported **potassium lead cobaltic nitrite,** $3K_2O.3PbO.2Co_2O_3.10N_2O_3.4H_2O$, obtained by the action of a mol of nitrous acid on a mol of cobalt sulphate and three mols of lead acetate, sulphate, or nitrate. The soln. is then treated with acetic or nitric acid, and the soln. slowly deposits crystals of the triple salt. A. Rosenheim and I. Koppel could not verify this. They obtained **cobaltous cobaltic oxynitritonitrate,** $2CoO.Co_2O_3.3N_2O_3+Co(NO_3)_2.14H_2O$, in small black crystals, by treating cobalt carbonate suspended in water with nitrous acid, and allowing the brown soln. to evaporate at ordinary temp.

O. L. Erdmann prepared some triple nitrites of bivalent cobalt. Thus, **potassium calcium cobalt nitrite,** $2KNO_2.Ca(NO_2)_2.Co(NO_2)_2$; **potassium strontium cobalt nitrite,** $2KNO_2.Sr(NO_2)_2.Co(NO_2)_2$; and **potassium barium cobalt nitrite,** $2KNO_2.Sr(NO_2)_2.Co(NO_2)_2$. V. Cuttica and M. Paoletti said that these compounds form dirty yellow powders stable in air and may be regarded as salts of one and the same complex quadrivalent ion, $Co(NO_2)_6$. The latter is, however, not stable in presence of water, in contact with which the salts yield an insoluble golden-yellow compound, $K_2Co(NO_2)_4$, the stable cobaltonitrous ion being hence $[Co(NO_2)_4]''''$. The high value of the active mass of the ion $[NO_2]'$ present in the conditions of the reaction in which the triple salt originates tends to displace the equilibrium $[Co(NO_2)_4]''+2NO_2' \rightleftharpoons [Co(NO_2)_6]''''$ towards the right, a displacement in the same sense, that is, towards the formation of undissociated mols. of the triple nitrite, being determined also in the equilibrium

$$[Co(NO_2)_6]^{Zn}_{K_6}$$

They prepared **barium thallium cobalt nitrite,** $Co(NO_2)_2.2Ba(NO_2)_2.TlNO_2$; **sodium barium cobalt nitrite,** $Co(NO_2)_2.2Ba(NO_2)_2.NaNO_2$, as a dirty green powder; **potassium zinc cobalt nitrite,** $2Co(NO_2)_2.Zn(NO_2)_2.6KNO_2$, as a dirty yellow powder; **potassium cadmium cobalt nitrite,** $2Co(NO_2)_2.Cd(NO_2)_2.6KNO_2$, as a pale chestnut-brown powder; and **potassium mercuric cobalt nitrite,** $Co(NO_2)_2.Hg(NO_2)_2.6KNO_2$, as a deep chestnut-brown powder. V. Cuttica and F. Gallo prepared potassium cerous cobalt nitrite, $2Co(NO_2)_2.Ce(NO_2)_3.5KNO_2$, as a green powder decomposed by water; rubidium cerous cobalt nitrite, $2Co(NO_2)_2.Ce(NO_2)_3.5RbNO_2$, is green, and thallous cerous cobalt nitrite,

$2Co(NO_2)_2.Ce(NO_2)_3.5ThNO_2$, is deep brown. The compounds are decomposed by water and by cold dil. acids. They can be represented by the general formula:



$$[Co(NO_2)_6]_2{}^{Ce}_{K_5}$$

where Ce represents Ce, La, Pr, Nd, or Y atoms, and K represents K, Rb, or Tl atoms. V. Cuttica prepared **potassium lead cobalt nitrite,** $Co(NO_2)_2.Pb(NO_2)_2.2KNO_3$; **rubidium lead cobalt nitrite,** $Co(NO_2)_2.Pb(NO_2)_2.2RbNO_2$; **ammonium lead cobalt nitrite,** $Co(NO_2)_2.Pb(NO_2)_2.2NH_4NO_2$; and **thallium lead cobalt nitrite,** $Co(NO_2)_2.Pb(NO_2)_2.2TlNO_2$, as dark green, microcrystalline powders by mixing a neutral soln. of a cobaltous salt, a conc. soln. of a lead salt, and then a large excess of the alkali nitrate soln. The formation of the potassium lead cobaltous salt enables one part of potassium in 10,000 parts of soln. to be detected. S. M. Jörgensen prepared **cobaltic hexamminohexanitrite,** $[Co(NH_3)_6][Co(NO_2)_6]$, as a yellow powder by mixing soln. of cobaltic hexamminochloride, and sodium cobaltic nitrite. It is almost insoluble in water; and when treated with thallium sulphate gives scarlet-red *thallous cobaltic hexanitrite,* $[Co(NO_2)_6]Tl_3$. P. Jacobson prepared **cobaltic hexamminotrinitrite,** $[Co(NH_3)_6](NO_2)_3$, by the action of solid sodium nitrite on cobaltic hexamminotrichloride. This salt was also prepared by C. Duval. E. Birk, and W. Biltz studied the mol. vol.

S. M. Jörgensen made **cobaltic hexamminodiamminotetratrinitritocobaltiate,** $[Co(NH_3)_6]$-$[Co(NH_3)_2(NO_2)_4]_3$; **cobaltic nitratopentammine hexanitritocobaltiate,** $[Co(NH_3)_5(NO_3)]$-$[Co(NO_2)_6].2H_2O$; and **cobaltic nitratopentammine tetranitritodiamminocobaltiate,** $[Co(NH_3)_5$-$NO_3][Co(NH_3)_2(NO_2)_4]_2$; and A. Werner and H. Müller, **cobaltic isothiocyanatopentammine nitrite,** $[Co(NH_3)_5(SCN)](NO_2)_2$. C. Duval prepared **cobaltic aquopentamminonitrite,** $[Co(NH_3)_5(H_2O)](NO_2)_3$. For **cobaltic hydronitritoimidoctammine nitrate,** $\{Co_2(NH)(NH_3)_8$-$(HNO_2)\}(NO_3)_4.H_2O$, also the sulphate, and chloride, *vide supra,* amides; likewise also for **cobaltic hydronitritoimidohexamminotetrachloride,** $\{Co_2(NH)(NH_3)_6(HNO_2)\}Cl_4.H_2O$.

A series of cobaltic **nitritopentammines** were discovered by O. W. Gibbs in 1852, and investigated by O. W. Gibbs and F. A. Genth, in 1856. They applied the term *xantho-salts,* and they supposed the group $(\frac{1}{2}N_2O_3.\frac{1}{2}H_2O)$ was present. In 1864, C. D. Braun showed that the nitrite radicle is present. O. W. Gibbs made a further study of the series in 1875; and in 1899, S. M. Jörgensen showed that a series of isomeric salts can be produced, and he called the isomers, isoxantho-salts. He showed that in the xantho-salts, the NO_2-group is probably present as $—NO_2$, and in the isoxantho-salts, as $—O.NO$.

C. Duval prepared **cobaltic nitritopentamminonitrite, sulphatopentamminonitrite, carbonatopentamminonitrite, and oxalatopentamminonitrite.** J. Meyer and H. Moldenhauer prepared **cobaltic nitritopentamminoselenate,** $[Co(NO_2)(NH_3)_5]SeO_4$. By boiling cobaltic aquopentammine sulphate with barium nitrite, O. W. Gibbs obtained **cobaltic nitritopentamminodinitrite,** $[Co(NH_3)_5NO_2](NO_2)_2.2H_2O$; if cobaltic chloropentamminochloride is treated with silver nitrite, **cobaltic silver nitritopentamminodinitrite,** $[Co(NH_3)_5NO_2](NO_2)_2.AgNO_2$, is formed. S. M. Jörgensen, O. W. Gibbs, and S. P. Sadtler made **cobaltic nitritopentamminohexanitritocobaltiate,** $[Co(NH_3)_5NO_2]_3[Co(NO_2)_6]_2$, by the action of sodium hexamminocobaltiate, on the nitritopentamminochloride; and **cobaltic nitritopentammine tetranitritodiamminocobaltiate,** $[Co(NH_3)_5NO_2][Co(NH_3)_2(NO_2)_4]_2$, was also prepared. O. W. Gibbs and F. A. Genth made **cobaltic nitritopentamminosulphate,** $[Co(NH_3)_5NO_2]SO_4$, by the action of nitrous fumes on an ammoniacal soln. of cobalt sulphate. Its properties were also investigated by S. M. Jörgensen, and C. D. Braun. **Cobaltic nitritopentamminohydrosulphate,** $[Co(NH_3)_5NO_2]SO_4.H_2SO_4$, was also examined by S. M. Jörgensen. W. Gibbs and F. A. Genth, and S. M. Jörgensen prepared **cobaltic nitritopentamminodichloride,** $[Co(NH_3)_5NO_2]Cl_2$. It is obtained by the action of the sulphate of the series on barium nitrite. The properties were studied by F. M. Jäger, A. Werner and C. H. Herty, A. Werner and A. Miolati, and E. Petersen. N. Schiloff and B. Nckrassoff studied the adsorption of the complex salt by activated charcoal. The isomer, **cobaltic isonitritopentamminodichloride,** $[Co(NH_3)_5O.NO]Cl_2$, was also prepared by S. M. Jörgensen by warming cobaltic chloropentamminodichloride with water and ammonia; the filtered liquid is cooled and neutralized with dil. hydrochloric acid; a soln. of sodium nitrite and hydrochloric acid is next added, and the red isomeride is precipitated; it is converted into the normal salt by dissolving it in water containing a few drops of ammonia, and precipitating with conc. hydrochloric acid. The iso-salt is about 4 times as soluble in cold water as the normal salt. Complex salts of the normal chloride with *mercuric chloride*, *auric chloride*, and *platinic chloride* were examined by O. W. Gibbs, O. W. Gibbs and F. A. Genth, and S. M. Jörgensen. O. W. Gibbs, O. W. Gibbs and F. A. Genth, C. D. Braun, S. M. Jörgensen, and E. Petersen examined **cobaltic nitritopentamminodinitrate**, $[Co(NH_3)_5NO_2](NO_3)_2$; O. W. Gibbs, **cobaltic nitritopentammine nitratochloroaurate**, $[Co(NH_3)_5NO_2]NO_3(AuCl_4)$, and likewise **cobaltic nitritopentammine nitratochloroplatinate**, $[Co(NH_3)_5NO_2]_2(NO_3)_2(PtCl_6)$; O. W. Gibbs, and F. M. Jäger, **cobaltic nitritopentammine chloronitrate**, $[Co(NH_3)_5NO_2](NO_3)Cl$; O. W. Gibbs, and A. Werner and A. Miolati, **cobaltic nitritopentammine dibromide**, $[Co(NH_3)_5NO_2]Br_2$; O. W. Gibbs, **cobaltic nitritopentammine bromonitrate**, $[Co(NH_3)_5NO_2](NO_3)Br$; C. D. Braun, **cobaltic nitritopentammine diiodide**, $[Co(NH_3)_5NO_2]I_2$; O. W. Gibbs, **cobaltic nitritopentammine sulphatoiodide**, $[Co(NH_3)_5NO_2]_2(SO_4)I_2.2H_2O$; and **cobaltic nitritopentammine sulphatoperiodide**, $[Co(NH_3)_5NO_2](SO_4)I_2$; S. M. Jörgensen made **cobaltic nitritopentammine fluosilicate**, $[Co(NH_3)_5NO_2]SiF_6$; O. W. Gibbs, **cobaltic nitritopentammine chromate**, $[Co(NH_3)_5NO_2]CrO_4.H_2O$; and **cobaltic nitritopentammine dichromate**, $[Co(NH_3)_5NO_2]Cr_2O_7.H_2O$. W. Flügel prepared **cobaltic nitritopentamminoamidosulphonate**, $[Co(NH_3)_5(NO_2)](NH_2SO_3)_2$, as well as the **imidosulphonate, hydroxynitritomonosulphonate, hydroxynitritodisulphonate, iso-hydroxynitritodisulphonate**, and **nitritotrisulphonate**. O. W. Gibbs, O. W. Gibbs and F. A. Genth, and C. D. Braun prepared the *ferrocyanide ;* and O. W. Gibbs and F. A. Genth, C. D. Braun, and S. M. Jörgensen, the *oxalate*. P. R. Ray prepared **cobaltic nitritopentamminothiosulphate**, $[Co(NH_3)_5(NO_2)]S_2O_3$, by passing air into an ammoniacal soln. of cobalt hydroxide, ammonium thiosulphate, and sodium nitrite.

In 1894, S. M. Jörgensen discovered the **nitritoaquotetrammines** ; and a few years later, A. Werner and R. Klein prepared some members of the series. These salts are like the nitritopentammines with one ammonia mol. replaced by a mol. of water ; they can therefore be regarded as aquoxantho-salts.

S. M. Jörgensen examined **cobaltic nitritoaquotetrammine tetranitritodiamminocobaltiate**, $[Co(NH_3)_4(H_2O)(NO_2)][Co(NH_3)_2(NO_2)_4]_2$; **cobaltic nitritoaquotetramminonitrite**, $[Co(NH_3)_4(H_2O)(NO_2)][Co(NH_3)_2(NO_2)_4]_2$; **cobaltic nitritoaquotetramminosulphate**, $[Co(NH_3)_4(H_2O)(NO_2)]SO_4$; S. M. Jörgensen, and A. Werner and C. H. Herty, **cobaltic nitritoaquotetramminodichloride**, $[Co(NH_3)_4(H_2O)(NO_2)]Cl_2$; S. M. Jörgensen, a basic chloride, and a chloroaurate; S. M. Jörgensen, **cobaltic nitritoaquotetramminodibromide**, $[Co(NH_3)_4(H_2O)(NO_2)]Br_2$; A. Werner and R. Klein, **cobaltic nitritoaquotetramminodiiodide**, $[Co(NH_3)_4(H_2O)(NO_2)]I_2$; A. Werner and R. Klein, **cobaltic nitritoaquotetramminocarbonate**, $[Co(NH_3)_4(H_2O)(NO_2)]CO_3$; J. Meyer and H. Moldenhauer prepared **cobaltic cis-dinitritotetramminoselenate**, $[Co(NO_2)_2(NH_3)_4]_2SeO_4$, as well as **cobaltic trans-dinitritotetramminoselenate** respectively from flavo- and croceo-cobaltic chloride and silver selenate; J. Meyer and K. Gröhler, **cobaltic aquonitritotetramminohydrosulphate**, $[(NH_3)_4Co(H_2O)(NO_2)](HSO_4)_2$; **cobaltic aquonitritotetramminohydroselenate**, $[(NH_3)_4Co(H_2O)(NO_2)](HSeO_4)_2$; and **cobaltic aquonitritotetramminoselenate**, $[(NH_3)_4Co(H_2O)(NO_2)]SeO_4$. S. M. Jörgensen, and A. Werner and R. Klein also made an *oxalate* and a *tartrate*.

In 1875, O. W. Gibbs made a series of **dinitritotetrammines** under the name *croceo-salts ;* and S. M. Jörgensen, in 1894, made a series of isomeric dinitritotetrammines which he called *flavo-salts*. A. Werner showed that the two series of salts are probably structurally alike, and are probably analogous to the cis- and trans- forms of nitrous acid. The solubilities of several of these salts were by J. N. Brönsted and A. Petersen, by V. K. la Mer and C. F. Mason, and by F. Ephraim.

S. M. Jörgensen, and A. Werner and A. Miolati examined **cobaltic trans-dinitritotetramminonitrite**, $[Co(NH_3)_4(NO_2)_2]NO_2$; **cobaltic cis- and trans-dinitritotetrammine hexanitritocobaltiate**, $[Co(NH_3)_4(NO_2)_2][Co(NO_2)_6]$—the former is dihydrated, the latter anhydrous ; **cobaltic cis- and trans-dinitritotetrammine tetranitritodiamminocobaltiate**, $[Co(NH_3)_4(NO_2)_2]Co(NH_3)_2(NO_2)_4]$; S. M. Jörgensen, A. Werner and A. Miolati, A. Werner and C. H. Herty, and E. Petersen, **cobaltic cis- and trans-dinitritotetramminonitrate**, $[Co(NH_3)_4(NO_2)_2]NO_3$; a *cis-hydronitrate* and a *cis-potassium nitrate* were also prepared ; S. M. Jörgensen, and A. Werner and A. Miolati, **cobaltic cis- and trans-dinitritotetramminosulphate**, $[Co(NH_3)_4(NO_2)]_2SO_4$; S. M. Jörgensen, and A. Werner prepared the cis-salt; and O. W. Gibbs, A. Werner, S. M. Jörgensen, F. M. Jäger, A. Werner and A. Miolati, and A. Werner and C. H. Herty, the trans-salt of **cobaltic dinitritotetramminochloride**, $[Co(NH_3)_4(NO_2)_2]Cl$. N. Schiloff and B. Nekrassoff studied the adsorption of the salt by activated charcoal. S. M. Jörgensen made the *cis-chloroaurate*, the *cis-chloroplatinite*, and the *cis-chloroplatinate*, while O. W. Gibbs made the *trans-chloroaurate*, and *trans-chloroplatinate*. O. W. Gibbs made **cobaltic trans-dinitritotetramminobromide**, $[Co(NH_3)_4(NO_2)_2]Br$; and **cobaltic trans-dinitritotetramminoperiodide**, $[Co(NH_3)_4(NO_2)_2]I_3$. F. Ephraim and P. Mosimann studied the *polyiodides* of the cis-and trans-salts, and also **bismuth cobaltic dinitritotetramminoiodide**, $[Co(NH_3)_4(NO_2)_2]I.BiI_3$. The **perchlorate**, and **selenate** were also prepared. S. M. Jörgensen prepared the cis-salts, and O. W. Gibbs the trans-salts of **cobaltic dinitritotetramminochromate**, $[Co(NH_3)_4(NO_2)_2]_2CrO_4$, and **cobaltic dinitritotetramminodichromate**, $Co(NH_3)_4(NO_2)_2]_2Cr_2O_7$. W. Flügel prepared *cis-* and *trans*-salts of **cobaltic dinitritotetramminonitrilotrisulphonate**, $[Co(NH_3)_4(NO_2)_2]_3N(SO_3)_3$, and also the *cis-* and *trans*-**iso-nitritodisulphonates**, and **amidosulphonates**.

A. Werner and co-workers prepared a series of **dinitritodiethylenediamines** in what are probably two stereoisomeric forms. The cis-series corresponds with the flavo-salts, and the trans-series with the croceo-salts. In the formulæ, for the sake of brevity, en, or En, is written in place of ethylenediammine. A. Werner also made the trans-salts with pyridine in place of ethylenediammine.

A. Werner and E. Humphrey prepared **cobaltic cis- and trans-dinitritodiethylenediamino nitrite**, $[Coen_2(NO_2)_2]NO_2$; A. Werner and E. Humphrey, **cobaltic cis- and trans-dinitritodiethylenediamine nitrate**, $[Coen_2(NO_2)_2]NO_3$; A. Werner and E. Humphrey, **cobaltic cis-dinitritodiethylenediamine sulphate**, $[Coen_2(NO_2)_2]_2SO_4$; A. Werner and E. Humphrey, and L. Gerb, **cobaltic cis- and trans-dinitritodiethylenediamine chloride**, $[Coen_2(NO_2)_2]Cl$, as well as a *cis-chloroaurate*, and *cis- and trans-chloroplatinites*, and *cis- and trans-chloroplatinates*; A. Werner and E. Humphrey, and F. M. Jäger, **cobaltic cis- and trans-dinitritodiethylenediamine bromide**, $[Coen_2(NO_2)_2]Br$; and **cobaltic cis- and trans-dinitritodiethylenediamine iodide**, $[Coen_2(NO_2)_2]I$. A. Werner and L. Gerb also made **cobaltic cis- and trans-nitritonitratodiethylenediamine nitrate**, $[Coen_2(NO_2)(NO_3)]NO_3$. A. Werner also made **cobaltic cis- and trans-dinitritodiethylenediamine dithionate**, $[Coen_2(NO_2)_2]_2S_2O_6$.

In 1901, A. Werner prepared **chloronitritodiethylenediamines** in stereoisomeric forms. The cis-series corresponds with the flavo-salts, and the trans-series with the croceo-salts.

A. Werner, and A. Werner and L. Gerb described **cobaltic cis-nitritochlorodiethylenediamine nitrite**, $[Coen_2Cl(NO_2)]NO_2$; **cobaltic cis- and trans-nitritochlorodiethylenediamine nitrate**, $[Coen_2Cl(NO_2)]NO_3$—the crystals of the trans-salts were also examined by F. M. Jäger; and A. Werner prepared an *acid cis-nitrate*. A. Werner and L. Gerb prepared **cobaltic cis-nitritochlorodiethylenediamine hydrosulphate**, $Coen_2Cl(NO_2)HSO_4$; A. Werner and L. Gerb, **cobaltic cis- and trans-nitritochlorodiethylenediamine chloride**, $[Coen_2Cl(NO_2)]Cl$; likewise also the two *bromides*, the two *iodides*, and the two *thiocyanates*. C. Duval prepared **cobaltic cis- and trans-dinitrotetramminonitrite, trans-dichlorotetramminonitrite, cis- and trans-dichlorotetramminonitrite, cis- and trans-diiodotetramminonitrite, chloronitrotetramminonitrite, diaquotetramminonitrite, and chloroaquotetramminonitrite.**

S. M. Jörgensen prepared **cobaltic hydroxynitritotetramminochloride**, $[Co(NH_3)_4(NO_2)(OH)]Cl.H_2O$. A. Werner showed that the original idea that the salt was a basic chloride, $[Co(NH_3)_2(H_2O)(NO_2)]Cl(OH)$, was wrong. A. Werner prepared a *hydrochloride*, a *bromide*, a *hydrobromide*, a *hydroiodide*, and a *nitrate*. A. Werner prepared **cobaltic nitritohydrocarbonatotetramminonitrate**, $[Co(NH_3)_4(NO_2)(HCO_3)]NO_3.H_2O$, by passing carbon dioxide into a soln. of cobaltic hydroxynitritotetramminonitrate. The dark yellow crystals are almost insoluble in water. A. Werner and R. Klein prepared a series of **cobaltic nitritothiocyanatotetrammines**—*e.g.* $[Co(NH_3)_4(NO_2)(SCN)]Cl$, in addition to the chloride, the bromide, iodide, periodide, nitrate, and thiocyanate, as well as complexes with mercuric chloride, and silver nitrate. A. Werner and L. Gerb made **cobaltic nitritothiocyanatodiethylenediamines**—*e.g.* **cobaltic nitritothiocyanatodiethyldiamminochloride**, $[Coen_2(NO_2)(SCN)]Cl$, as well as the bromide, iodide, and nitrate. S. M. Jörgensen, and K. A. Hofmann and S. Reinsch prepared **cobaltic nitritosulphitotetrammine**, $[Co(NH_3)_4(NO_2)(SO_3)]$.

In 1866, O. L. Erdmann discovered the first of a series of **trinitritotriammines**, and the other members of the series were studied by O. W. Gibbs in 1875, and S. M. Jörgensen in 1894. The first member, **cobaltic trinitritotriammine**, or cobaltic triamminonitrite, $[Co(NH_3)_3(NO_2)_3]$, was obtained by O. L. Erdmann, P. R. Rey, and by W. Gibbs. S. M. Jörgensen prepared it by the following process: cobalt carbonate (10 grms.), dissolved in hydrochloric acid (50 c.c.), was treated with varying quantities of sodium nitrite and 20 per cent. ammonia and the mixture oxidized in various ways; the dark brown liquor obtained was filtered from the insoluble matter, and evaporated to dryness in a draught. The residue was dissolved in 50–70 c.c. of cold water, whereby a second residue was obtained, and a dark brown soln. which, when treated with dil. nitric acid, yielded the xanthonitrate. The insoluble residues were washed with cold water until free from chlorine, whereby the croceo- and xantho-chlorides were removed, and the residue free from chlorine was extracted with hot water containing some acetic acid, when the triamine nitrite was dissolved. This was separated from the croceo-diamine nitrite and other sparingly soluble impurities by fractional crystallization from very dil. acetic acid; the bulk of the croceo-diammine nitrite was obtained in the last extraction of the residues.

A. Werner thought that the compound existed in two isomeric forms, but S. M. Jörgensen showed that the alleged isomers are the results of difficulties in the habits of the crystals of one compound—if crystallized from dil. acetic acid at 66°, rhombic plates are formed; and at 85°, hot aq. or conc. acetic acid soln. give yellowish-brown needles. H. Jäger gave for the axial ratios of the rhombic bisphenoids, $a:b:c=0{\cdot}8682:1:0{\cdot}6020$. The sp. gr. is 2·020 at 17°. The salt is sparingly soluble in cold water, readily soluble in hot water. The aq. soln. does not give the usual reactions for the nitrites. W. Biltz, and E. Birk studied the mol. vol. The electrical conductivity was measured by A. Werner and co-workers, and E. Petersen. These compounds have not the general characters of ordinary salts. N. Schiloff and B. Nekrassoff studied the adsorption of the salt by activated charcoal.

There are a number of other members of the series. Thus, A. Werner and A. Grün prepared **cobaltic trinitritoethylenediaminammine**, $[Co(NH_3)en(NO_2)_3]$; S. M. Jörgensen, **cobaltic sulphatobisdinitritobistriammine**, $[(NH_3)_3(NO_2)_2Co(SO_4)Co(NO_2)_2(NH_3)_3]$; S. M. Jörgensen, and A. Werner, **cobaltic dinitritochlorotriammine**, $[Co(NH_3)_3Cl(NO_2)_2]$, which was examined by A. Werner and A. Miolati, and E. Petersen; S. M. Jörgensen, **cobaltic dinitritobromotriammine**, $[Co(NH_3)_3Br(NO_2)_2]$; A. Werner, **cobaltic nitritoxalatotriammine**, $[Co(NH_3)_3(C_2O_4)(NO_2)]$; and L. A. Tschugaeff, **cobaltic nitritodimethylglyoximammine**, $[Co(NH_3)(NO_2)(D_2H_2)]$, where D_2H_2 stands for dimethylglyoxime.

O. L. Erdmann prepared **tetranitritodiamminocobaltiates** in 1866, and these products are sometimes called Erdmann's salts—usually the ammonium salt. They were studied by O. W. Gibbs, who proved that the cobalt forms part of the negative radicle. A. Werner represented these salts by the general formula $M[Co(NH_3)_2(NO_3)_4]$, and considered them to be *ein wichtiges Uebergangsgleid*, between the neutral trinitritotriammines, $[Co(NH_3)_3(NO_2)_3]$, and the hexanitritocobaltiates, $M_3Co(NO_2)_6$. These salts were also studied by S. M. Jörgensen, and A. Werner and fellow-workers. J. N. Brönsted and A. Petersen measured the solubilities of some of these salts; and S. Berkman and H. Zocher, their magnetic susceptibilities. O. L. Erdmann, and O. W. Gibbs made **ammonium tetranitritodiamminocobaltiate**, $NH_4[Co(NH_3)(NO_2)_4]$, by the spontaneous evaporation of mixed soln. of neutral cobaltous chloride, and ammonium nitrite.

S. M. Jörgensen mixed a soln. of 90 grms. of crystallized cobaltous chloride at 250 c.c. of water with a soln. containing 100 grms. of ammonium chloride, 135 grms. crystal sodium nitrite, and 750 c.c. of water along with 25 c.c. of 20 per cent. aq. ammonia. The mixture was treated for 1½ hrs. with a rapid current of air. The filtered liquid was allowed to stand 14 days exposed to air. The liquid was decanted from the crystals, the latter were washed by suction—once with iced-water, and once with a soln. of the pure salt. The mother-liquor mixed with the wash-water deposits another crop of crystals after standing some time exposed to air.

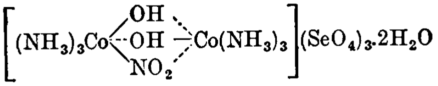
The brown rhombic prisms were shown by F. M. Jäger to have the axial ratios $a:b:c=0{\cdot}8837:1:0{\cdot}5226$; and a sp. gr. 1·933 at 15°. The salt develops ammonia when treated with potassium hydroxide. This salt can be used as a starting point for the preparation of some other ammines. According to S. M. Jörgensen, with ammonia, it forms the cobaltic dinitritotetrammine tetranitritodiamminocobaltiate. O. L. Erdmann prepared **potassium tetranitritodiamminocobaltiate**, $K[Co(NH_3)_2(NO_2)]$, by adding potassium nitrite to a soln. of cobaltous and ammonium chlorides. The salt was also prepared by O. W. Gibbs, S. M. Jörgensen, and A. Werner. According to F. M. Jäger, the brown crystals belong to the rhombic system and have the axial ratios $a : b : c = 0\cdot8783 : 1 : 0\cdot5192$, and a sp. gr. 2·076 at 15°. The soln. in water is dark yellow, and it gives no precipitate with potassium hydroxide or ammonium carbonate. With ammonia the potassium salt reacts like the ammonium salt. R. Kremann studied the transport numbers; and A. Werner and A. Miolati, the electrical conductivity. Sodium tetranitritodiamminocobaltiate, $Na[Co(NH_3)_2(NO_2)_4]$, was also prepared. N. Schiloff and B. Nekrassoff studied the adsorption of the salt by activated charcoal.

S. M. Jörgensen obtained the closely similar salts, **rubidium tetranitritodiamminocobaltiate**, $Rb[Co(NH_3)_2(NO_2)_4]$; and **cæsium tetranitritodiamminocobaltiate**, $Cs[Co(NH_3)_2(NO_2)_4]$. O. L. Erdmann, O. W. Gibbs, and S. M. Jörgensen prepared **silver tetranitritodiamminocobaltiate**, $Ag[Co(NH_3)_2(NO_2)_4]$, as an orange-yellow precipitate by treating the potassium salt with silver nitrate. The salt can be recrystallized in needles or plates from its aq. soln. O. W. Gibbs prepared **mercurous tetranitritodiamminocobaltiate**, $Hg[Co(NH_3)_2(NO_2)_4]$, in orange-yellow crystals, presumably with the composition just indicated; similar remarks apply to the prismatic crystals of **thallous tetranitritodiamminocobaltiate**, $Tl[Co(NH_3)_2(NO_2)_4]$, and the orange-brown plates of **lead tetranitritodiamminocobaltiate**, $Pb[Co(NH_3)_2NO_2)_4]_2$, prepared by O. W. Gibbs. A. Werner and A. Gubser prepared **chromium dichlorotetraquatetranitritodiamminocobaltiate**, $Cr(H_2O)_4Cl_2[Co(NH_3)_2(NO_2)_4].2H_2O$, in yellowish-green plates, by the action of chromium chlorohydroxide on potassium tetranitritodiamminocobaltiate. The corresponding **chromium dibromotetraquotetranitritodiamminocobaltiate** was made in dark green crystals, in a corresponding way. A. Werner and D. Kalkmann also prepared **chromium hexacarbamide tetranitritodiamminocobaltiate**, $Cr(CON_2H_4)_6[Co(NH_3)_2(NO_2)_4]_3.H_2O$; and **chromium chlorohexacarbamide tetranitritodiamminocobaltiate**, $Cr(CON_2H_4)_6Cl[Co(NH_3)_2(NO_2)_4].3H_2O$. O. W. Gibbs, and S. M. Jörgensen prepared **cobaltihexammine tetranitritodiamminocobaltiate**, $[Co(NH_3)_6][Co(NH_3)_3(NO_2)_4]$; **cobaltinitritopentammine tetranitritodiamminocobaltiate**, $[Co(NH_3)_5NO_2]Co(NH_3)_2(NO_2)_4]$; S. M. Jörgensen, **cobaltinitritoaquotetrammine tetranitritodiamminocobaltiate**, $[Co(NH_3)_4(H_2O)(NO_2)][Co(NH_3)_2(NO_2)_4]$; S. M. Jörgensen, **cobalticis- and trans-dinitritotetrammine tetranitritodiamminocobaltiate**, $[Co(NH_3)_4(NO_2)_2][Co(NH_3)_2(NO_2)_4]$, the electrical conductivity was measured by A. Werner and A. Miolati; S. M. Jörgensen, and O. W. Gibbs, **cobaltinitratopentammine tetranitritodiamminocobaltiate**, $[Co(NH_3)_5NO_3][Co(NH_3)_2(NO_2)_4]$; and A. Werner, **cobaltidichloroaquotriammine tetranitritodiamminocobaltiate**, $[Co(NH_3)_3(H_2O)Cl_2][Co(NH_3)_2(NO_2)_4]$; K. A. Hofmann and K. Buchner prepared **toluidine tetranitritodi-p-toluidinocobaltiate**, $CH_3.C_6H_4.NH_2.H[Co(CH_3.C_6H_4.NH_2)_2(NO_2)_2]$, and also **sodium tetranitratodinitrosohydrazinocobaltiate**, $Na[Co(NO_2)_4(NO.NH)_2]$. F. Ephraim and F. Moser prepared **copper tetranitrohexamminocobaltiate**, $[Cu(NH_3)_4][(NO_2)_4Co(NH_3)_2]_2$; **zinc tetranitritoheptamminocobaltiate**, $[Zn(NH_3)_4][(NO_2)_4Co(NH_3)_2]_2$; **nickel tetranitritohexamminocobaltiate**, $[Ni(NH_3)_4][(NO_2)_4Co(NH_3)_2]_2$; **copper oxalatodinitritohexamminocobaltiate**, $[Cu(NH_3)_4][(C_2O_4)(NO_2)_2Co(NH_3)_2]_2$; **zinc oxalatodinitritohexamminocobaltiate**, $[Zn(NH_3)_4][(C_2O_4)(NO_2)_2Co(NH_3)_2]_2$; **cadmium oxalatodinitritohexamminocobaltiate**, $[Cd(NH_3)_4][(C_2O_4)(NO_2)_2Co(NH_3)_2]_2$; and **nickel oxalatodinitritodecamminocobaltiate**, $[Ni(NH_3)_8][(C_2O_4)(NO_2)_2Co(NH_3)_2]_2$.

S. M. Jörgensen prepared a salt of the **dinitritodichlorodiamminocobaltiates** where the acidic radicle is univalent. The complex obtained was **cobaltinitritochlorotetrammine dinitritodichlorodiamminocobaltiate**, $[Co(NH_3)_4(NO_2)Cl][Co(NH_3)_2(NO_2)_2Cl_2]$. S. M. Jörgensen also prepared a series of **dinitrito-oxalatodiamminocobaltiates** represented by the *ammonium* salt, $NH_4[Co(NH_3)_2(NO_2)_2(C_2O_4)]$. The *potassium, sodium, barium, magnesium, silver, cobalt, cobalt silver, cobalthexammine*, and *cobaltidinitritotetrammine dinitritoxalatodiamminocobaltiates* were also prepared. L. A. Tschugaeff prepared a series of **dinitritodimethylglyoximinocobaltiates**, and **dinitritodimethylglyoximinocobaltic acid**, $H[Co(NO_2)_2Di_2H_2].H_2O$. The *ammonium, ethylammonium, diisobutylammonium, potassium, rubidium, cæsium*, and *sodium salts* were made. S. M. Jörgensen also made **ammonium oxalatobisdinitritobisdiamminocobaltiate**, $NH_4[(NH_3)_2(NO_2)_2Co.C_2H_4.Co(NO_2)_2(NH_3)_2]$. J. J. Meyer and co-workers prepared **dicobaltic tetranitrito-μ-selenatohexammine**, $[(NH_3)_3(NO_2)_2Co.O.SeO_2.O.Co(NO_2)_2(NH_3)_3].2H_2O$; **dicobaltic μ-amidonitritooctamminoselenate**:

$$\left[(NH_3)_4Co\!<\!\begin{smallmatrix}NO_2\\NH_3\end{smallmatrix}\!>\!CO(NH_3)_4\right](SeO_4)_2.2H_2O$$

and **dicobaltic μ-nitritodihydroxyhexamminoselenate:**



$$\left[(NH_3)_3Co\begin{matrix}OH\\OH\\NO_2\end{matrix}Co(NH_3)_3\right](SeO_4)_3.2H_2O$$

J. Lang found that the filtrate obtained from mixed soln. of barium nitrite and nickel sulphate can be evaporated without decomposition if the temp. be not raised. W. Hampe said that the soln. deposits a basic salt, *nickel oxynitrite*, $Ni_2O(NO_2)_2$. The reddish-yellow crystals of **nickelous nitrite,** $Ni(NO_2)_2$, are stable in air and at 100°. C. Duval obtained the salt as in the corresponding case of cobalt nitrite (*q.v.*). The salt forms a green soln. with water which gives no precipitate with alcohol. The aq. soln. decomposes at 80°–90°, and if then mixed with alcohol, dil. potash-lye decomposes the dry salt. When treated with ammonia, it forms a blue soln. P. C. Ray and N. R. Dhar found the electrical conductivities of soln. with a mol of the salt in 18·17, 54·51, 163·53, and 490·59 litres to be respectively 57·32, 78·52, 95·35, and 114·12 at 20°, when the calculated value at infinite dilution is 94. The aq. soln. is feebly acid to litmus. According to O. L. Erdmann, mixed soln. of ammonium nitrite and nickel acetate give an unstable green liquid, which remains clear when mixed with much alcohol, but on standing for a long time gives red crystals, which form more quickly in ammoniacal soln., or if absolute alcohol in excess be added. The product is considered to be **nickel tetramminodinitrite,** $Ni(NO_2)_2.4NH_3$. L. Soret and F. Robineau prepared a similar salt. Aq. ammonia of sp. gr. 0·924 (3 kilos.) and sodium nitrite (1 kilo.) are added to the nickel sulphate (1 kilo.) dissolved in boiling distilled water (1 litre); the mixture is placed aside for 4–5 days, and the resulting crop of crystals, after washing, is recrystallized from a hot ammoniacal soln. The small red crystals were considered by O. L. Erdmann to belong to the monoclinic system; they form a green soln. with cold water, and on warming, the soln. becomes turbid, forming a green precipitate. The salt decomposes in moist air giving off ammonia, and becoming green. The salt is insoluble in alcohol, and is recrystallized by adding alcohol to the ammoniacal soln. The salt begins to decompose at 100°, giving off ammonia and becoming green; at a higher temp., nickel oxide alone remains.

N. W. Fischer prepared **potassium nickel hexanitrite,** $K_4Ni(NO_2)_4$, in brownish-red octahedral crystals from a mixed soln. of nickel and potassium nitrites. J. Lang, O. L. Erdmann, and W. Hampe employed an analogous process. J. Lang said that the dry salt decomposes before it melts, giving off acid and nitric oxide vapours. The salt forms a green aq. soln. It is stable in air, and can be obtained unchanged by evaporating the aq. soln. J. Lang said that the aq. soln. has a slight alkaline reaction, and only a small green precipitate is produced with a long boiling; W. Hampe said the aq. soln. decomposed before boiling begins. The salt is insoluble in absolute alcohol, but traces are dissolved by 90 per cent. alcohol. The salt forms a basic nitrate when boiled with alcohol. Hydrogen sulphide forms nickel sulphide when passed into the aq. soln. J. Lang did not produce crystals of **sodium nickel nitrite** from a mixed soln. of sodium and nickel nitrites. J. Lang obtained **barium nickel tetranitrite,** $Ba_2Ni(NO_2)_4$, by allowing a mixed soln. of barium nitrite and nickel acetate to stand for some hours. The pale red crystalline powder is more soluble in water than the potassium salt. O. L. Erdmann said that the salt gradually decomposes, forming nitric oxide, nitrogen peroxide, and a greenish mass. J. Lang observed no loss in weight at 100°. C. Przibylla tried the triple salts: *ammonium barium nickel nitrite*, as well as *ammonium strontium nickel nitrite*, and *ammonium calcium nickel nitrite*, but found the products are mixtures, not chemical individuals. J. Lang reported **potassium barium nickel nitrite,** $K_2BaNi(NO_2)_6$, to be formed by concentrating a mixed soln. of nickel acetate and potassium barium nitrite; and also by the action of barium acetate on potassium nickel nitrite; O. L. Erdmann obtained it by the action of an excess of potassium nitrite on a mixed soln. of barium and nickel chlorides. The brownish-yellow powder was stated by J. Lang to consist of microscopic tetragonal plates; O. L. Erdmann said that the salt separates from the hot soln. in microscopic cubes and octahedra. The salt is sparingly soluble in cold water, readily soluble, without apparent decomposition, in hot water. The aq. soln., however, decomposes when boiled, forming nitric oxide, and a basic nitrate. The salt is insoluble in alcohol. F. Ephraim prepared **cæsium barium nickel nitrite,** $Cs_2Ba[Ni(NO_2)_6]$, as an orange-brown powder very sparingly soluble in water. O. L. Erdmann, J. Persoz, and C. Przibylla prepared **potassium strontium nickel nitrite,** $K_2SrNi(NO_2)_6$, as in the case of the barium salt. O. L. Erdmann said the reddish-yellow salt consists of microscopic cubes, and loses no weight at 140°. C. Künzel, and O. L. Erdmann made **potassium calcium nickel nitrite,** $K_2CaNi(NO_2)_6$, from a mixed soln. of a nickel salt, calcium chloride, and potassium nitrite in excess. O. L. Erdmann obtained it from a mixture of calcium chloride and potassium nickel nitrite. The yellow salt consists of microscopic octahedra belonging to the cubic system. The salt is sparingly soluble in cold water, but readily soluble in hot water. The salt is decomposed when heated with water. It is insoluble in alcohol, and this reagent precipitates the salt from its aq. soln. There is no loss in wt. at 130°–140°. It melts with decomposition at a higher temp. giving off nitric oxide and nitrogen peroxide. V. Cuttica and G. Carobbi could not prepare *potassium magnesium nickel nitrite,* but they obtained a number of other triple nitrites. The salt $Ni(NO_2)_2.4KNO_2$ is regarded as being constituted $[Ni(NO_2)_6]K_4$, and it ionizes in water: $[Ni(NO_2)_6]K_4 \rightleftharpoons Ni(NO_2)_6'''' + 4K^{\cdot}$; and $[Ni(NO_2)_6]'''' \rightleftharpoons Ni(NO_2)_2 + 4NO'_2$ also occurs. They prepared **potassium zinc nickel nitrite,** $2[Ni(NO_2)_6]K_4.Zn(NO_2)_2$, as a flesh-red crystalline mass; V. Cuttica prepared pale yellow **potassium nickel cadmium nitrite,** $4KNO_2.2Cd(NO_2)_2.Ni(NO_2)_2$; and flesh-coloured **ammonium nickel cadmium nitrite,** $2NH_6NO_2.Cd(NO_2)_2.Ni(NO_2)_2$; V. Cuttica and G. Carobbi made **potassium mercuric nickel nitrite,** $[Ni(NO_2)_6]K_2Hg$, dark green crystals forming a green aq. soln. in which the salt produces seven ions per mol. V. Cuttica and A. Paciello prepared **thallous nickel nitrite,** or *thallous nickelonitrite,* $Tl_4[Ni(NO_2)_6]$, in stable flesh-red crystals which yield stable, green aq. soln. V. Cuttica prepared **potassium cerous nickel nitrite,** $5Ni(NO_2)_2.3Ce(NO_2)_3.13KNO_2$, as a flesh-red powder. V. Cuttica made brick-red **thallium nickel cadmium nitrite,** $4TlNO_2.2Cd(NO_2)_2.Ni(NO_2)_2$; V. Cuttica and G. Carobbi obtained **thallium mercuric nickel nitrite,** in orange-red crystals, $3Ni(NO_2)_2.Hg(NO_2)_2.6TlNO_2$, or $2Ni(NO_2)_2.Hg(NO_2)_2.8TlNO_2$, according to the conditions; and V. Cuttica and F. Gallo, **thallium cerous nickel nitrite,** $6Ni(NO_2)_2.2Ce(NO_2)_3.7TlNO_2$, as a pale chestnut-brown powder; V. Cuttica and G. Carobbi made impure **thallium uranyl nickel nitrite,** as a chestnut-brown powder. C. Przibylla prepared a brown crystalline powder of *barium thallous nickel nitrite,* which was probably a mixture. He prepared brownish-yellow **potassium lead nickel nitrite,** $K_2PbNi(NO_2)_6$, by mixing dil. soln. of the component nitrates with an excess of sodium nitrite; **ammonium lead nickel nitrite,** $(NH_4)_2PbNi(NO_2)_6$, was obtained in an impure state; and **thallous lead nickel nitrite** formed a brown powder consisting of particles almost cubical in shape. The index of refraction was high. V. Cuttica and G. Carobbi prepared **potassium cobalt nickel nitrite,** $2K_4[Co(NO_2)_6].[Co(NO_2)_6]K_2Ni$, as a greenish-yellow powder; and **thallium cobalt nickel nitrite,** $[Co(NO_2)_6]Tl_2Ni.4TlNO_2$, as a dark red powder.

W. C. Ball and H. H. Abram added 10 c.c. of bismuth nitrate soln. to 40 c.c. of a 50 per cent. soln. of sodium nitrite, and then a soln. of 5 grms. of ammonium nitrate and 2 grms. of nickel nitrate in 20 c.c. of water—all cooled to 0°—in a few minutes a yellowish-brown, microcrystalline powder of **ammonium nickel nitritobismuthite** was formed. The composition of different specimens varied considerably, and the salt slowly decomposes; it is quickly hydrolyzed by water. In an analogous manner, **potassium nickel nitritobismuthite,** $K_4NiBi_2(NO_3)_{12}.6H_2O$. was formed as an unstable, yellowish-brown, microcrystalline powder; similarly with **rubidium nickel nitritobismuthite,** $Rb_7Ni\{Bi(NO_2)_6\}_3.4H_2O$; **cæsium nickel nitritobismuthite,** $Cs_7Ni\{Bi(NO_2)_6\}_3.6H_2O$; and **thallous nickel nitritobismuthite,** $Tl_4Ni\{Bi(NO_2)_6\}_2$.

O. W. Gibbs[17] prepared **potassium ruthenium hexanitrite,** $K_3Ru(NO_2)_6$, from a soln. of the component salts. It is easily soluble in water, alcohol, and ether ; and with ammonium sulphide it gives a red soln. C. E. Claus said that the salt is sparingly soluble in water, and readily soluble in a soln. of potassium nitrite. A. Joly and co-workers prepared orange-red **potassium ruthenium pentanitrite,** $K_2Ru(NO_2)_5$, from a neutral soln. of potassium nitrite and ruthenium chloride in the calculated proportions. Yellow **potassium ruthenium oxydodecanitrite,** $K_8Ru_2O(NO_2)_{12}$, was also obtained from an alkaline soln. in the presence of an excess of alkali nitrite. This salt is sparingly soluble in water, and it separates with water of crystallization, but becomes anhydrous at 100°. It explodes in vacuo at 360°–440°, forming nitrogen and nitric oxide, and a residue, which, when leached with water, contains KRu_3O_8. L. Brizard found that crystals of **potassium ruthenium dihydroheptanitrite,** $K_3Ru_2H_2(NO_2)_7.4H_2O$, are formed when a dil. and slightly warm soln. of the complex chloride, $Ru_2H_2(NO)Cl_3.3KCl.2HCl$, slightly acidified with hydrochloric acid, is mixed with successive small quantities of potassium nitrite until liberation of nitrogen oxides ceases. The colour of the soln. changes from red to orange-yellow, and, after conc., it deposits crystals of the complex nitrite. This salt is very soluble in water, but almost insoluble in a concentrated soln. of potassium chloride. It becomes anhydrous at 100°, but does not begin to decompose much below 360° ; at this temp., however, decomposition is rapid. When heated with hydrochloric acid, it is rapidly reconverted into the double chloride from which it was formed. A. Joly and E. Leidié found that when a soln. of sodium nitrite is gradually added to a soln. of ruthenium chloride at 60°–80° until the liquid is neutral, an orange-red soln. is obtained, which, on cooling, deposits the **sodium ruthenium pentanitrite,** $Na_2Ru(NO_2)_5.2H_2O$, in orange-yellow, dichroic, monoclinic prisms, very soluble in water, from which they can be repeatedly recrystallized without decomposing. When heated with dil. hydrochloric acid, the salt yields the nitrosochloride, $Ru(NO)Cl_3,2NaCl$; when mixed with potassium hydroxide and sat. with chlorine, it gives off vapours of ruthenium peroxide. From 5 to 6 kilos. of this salt were obtained from 60 kilos. of iridium residues, rich in ruthenium, and hence sodium nitrite is of great service in the extraction of the metal from substances in which it is present in small quantity. The sodium salt at 360° or 440° yields the compound Na_2O,Ru_4O_9, which cannot be a mere mixture of the alkali oxide and the ruthenium oxide, since the latter would decompose at 440°. At a dull red heat, the nitrite yields the oxide RuO_2, which retains only a trace of alkali after being washed with boiling water. If the temp. is so high that the alkali nitrite fuses, the greater part of the ruthenium is converted into the ruthenate Na_2RuO_4.

C. E. Claus prepared **potassium rhodium hexanitrite,** $K_3Rh(NO_2)_6$, as an orange-yellow powder by boiling a soln. of rhodium chloride with an excess of potassium nitrite. The salt is sparingly soluble in water, and readily soluble in hot hydrochloric acid, or in an excess of potassium nitrite soln. The soln. in potassium nitrite is coloured dark red by ammonium sulphide. O. W. Gibbs prepared a complex salt of **potassium rhodium chloronitrite.** C. E. Claus prepared **sodium rhodium hexanitrite,** $Na_3Rh(NO_2)_6$, in a manner analogous to that employed for the potassium salt. It is a white powder consisting of microscopic octahedra. The salt is sparingly soluble in boiling water, and is slowly decomposed by hot conc. hydrochloric acid, and, according to J. Lang, it is rapidly decomposed by aqua regia. J. Lang obtained **barium rhodium dodecanitrite,** $Ba_3Rh_2(NO_2)_{12}$, from barium rhodium chloride and silver nitrite. The white powder consists of microscopic cubes and octahedra.

W. Manchot and A. Waldmüller found that when nitric oxide acts on a soln. of palladous nitrate the primary nitrosyl complex which is formed produces

palladous nitrite, $Pd(NO_2)_2$. J. Lang prepared **palladous diamminonitrite,** $Pd(NO_2)_2(NH_3)_2$, by evaporating the filtered soln. obtained by adding silver nitrite to a soln. of palladous diamminonitrite. An isomeric form is obtained from palladous oxide, potassium nitrite, and ammonia. There is also the complex salt $Pd(NH_3)_2(NO_2)_2Pd(NO_2)_2$, or $Pd(NH_3)(NO_2)_2$, **palladium amminonitrite,** produced when a hot soln. of palladous diamminochloride is treated with potassium palladous nitrite, and either cooled or evaporated so as to obtain yellow prismatic crystals. N. W. Fischer, and J. Lang prepared **potassium palladous tetranitrite,** $K_2Pd(NO_2)_4$, by treating soln. of palladous chloride or nitrate with an excess of potassium nitrite. A white powder separates from dil. soln., while conc. soln. furnish yellow prisms. The aq. soln. yields the **dihydrated potassium palladous tetranitrite,** $K_2Pd(NO_2)_4.2H_2O$, in plates which lose all their water in vacuo over potassium hydroxide. When heated, the salt decomposes. A yellow, crystalline precipitate of **silver palladous tetranitrite,** $Ag_2Pd(NO_2)_4$, is obtained by adding silver nitrate to a soln. of the potassium salt. It crystallizes from hot water in dark yellow prisms. A. Rosenheim and H. Itzig prepared trihydrated **potassium palladous iodonitrite,** $K_2PdI_2(NO_2)_2.3H_2O$, by saturating a conc. soln. of potassium nitrite with palladous iodide and allowing the mixture to crystallize over sulphuric acid. The salt crystallizes in purplish-red, prismatic needles, effloresces on exposure to the air, and decomposes when dissolved in water or treated with dil. acids, with precipitation of palladous iodide. **Potassium palladous oxalatonitrite,** $K_2Pd(NO_2)_2C_2O_3$, was also obtained by warming the preceding salt with a molecular proportion of oxalic acid, and it crystallizes in beautiful, yellow needles sparingly soluble in cold, but easily soluble in hot water. Yellow rhombic crystals of **potassium palladic hexanitrite,** $K_2Pd(NO_2)_6$, were prepared by E. Pozzi-Escot and H. C. Couquet by treating a soln. of palladic chloride with potassium nitrite and then with an excess of alkali hydroxide or aq. ammonia at a low temp. O. W. Gibbs prepared **hydrohexanitritoiridic acid,** $H_3Ir(NO_2)_6$, in pale yellow needles readily soluble in water. **Potassium iridic hexanitrite,** $K_3Ir(NO_2)_6.H_2O$, was obtained by the action of an excess of potassium nitrite or iridium chloride. The pale greenish-yellow crystals are easily soluble in water; the compound forms a complex salt with potassium iridium chloride, **potassium iridic chloronitrite,** $K_3Ir(NO_2)_6.K_3IrCl_6$. **Sodium iridic hexanitrite,** $Na_3Ir(NO_2)_6.H_2O$; the complex $Na_3Ir(NO_2)_6.Na_3IrCl_6$; **sodium iridic chloronitrite,** $Na_2IrCl(NO_2)_4.H_2O$; and **barium iridic chloronitrite,** $Ba_3Ir_2(NO_2)_2.Ba_3Ir_2Cl_{12}$, also have been prepared.

J. Lang,[18] and L. F. Nilson prepared **hydrotetranitritoplatinous acid,** $H_2Pt(NO_2)_4$, or *platinous hydronitrite,* $Pt(NO_2)_2.2HNO_2$, or $(HO.NO : NO.O)_2Pt$, by treating the barium salt with the calculated quantity of sulphuric acid, and evaporating the filtered soln. in vacuo, over sulphuric acid and sodium hydroxide. The salts are described below. The red microscopic prisms readily form hydroctonitritotriplatinous acid (*vide infra*). The crystals of hydrotetranitritoplatinous acid form a yellow aq. soln. with a feeble acidic reaction; the alcoholic soln. is colourless. The aq. soln. gives no precipitate with potassium chloride. The salts of this acid readily crystallize from conc. soln. They are very soluble in water. Most of them are stable at 100°, but part or all the water of crystallization is lost at that temp. There is the **potassium tetranitritoplatinite,** $2KNO_2.Pt(NO_2)_2$, or $[(NO_2)_2Pt(NO_2)_2]K_2$, and **potassium oxalatodinitritoplatinite,** $K_2C_2O_4.Pt(NO_2)_2$, or $K_2[(C_2O_4)Pt(NO_2)_2]$. L. F. Nilson obtained **platinous oxydihydrotetranitritoplatinite,** $PtO.H_2Pt(NO_2)_4$, represented by a series of salts—silver, beryllium, aluminium, indium, chromium, and iron (*vide infra*). **Hydroctonitritotriplatinous acid,** $H_4Pt_3O(NO_2)_8.2H_2O$, separated as a brown or green powder during the evaporation of the mother-liquor from the above acid. It gives off water but not nitrogen at 100°. It readily dissolves in water, forming a yellow acid-liquor which drives carbon dioxide from the carbonates. By saturating the acid with potassium carbonate, L. F. Nilson obtained **potassium oxyoctonitritotriplatinite,** $K_4Pt_3O(NO_2)_8.2H_2O$, in yellow plates, which are stable in air; and lose only their water of crystallization at 100°. The salt can be recrystallized from its aq. soln.

The sexibasic acid, **oxyhydrohexanitritoplatinous acid,** $H_6Pt_3O(NO_2)_6$, is represented by the **potassium oxyhexanitritoplatinite,** $K_2H_4Pt_3O(NO_2)_6.3H_2O$. M. Vèzes prepared it in small quantities by treating potassium tetranitritoplatinite with a halogen. The hot conc. soln. of potassium tetranitritoplatinite is titrated with an eq. amount of sulphuric acid, and the green soln. is heated; nitrous fumes are evolved, and, on cooling, dark red needles separate. The salt loses water slowly in cold dry air, rapidly at 100°. It dissolves sparingly in cold water, and readily in hot water; it is insoluble in alcohol. The aq. soln. is stable and reacts acid to litmus.

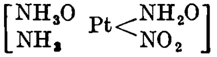
J. Lang prepared **platinous tetramminodinitrite,** $[Pt(NH_3)_4](NO_2)_2.2H_2O$, by the action of soln. of platinous tetramminodichloride and silver nitrite, and evaporating the filtrate at a low temp. The four-sided prisms effloresce in air, and are dehydrated over conc. sulphuric acid. At 145°, they lose 2 mols of ammonia, forming cis-platinous diamminodinitrite, $[Pt(NH_3)_2(NO_2)_2]$; and at 250°, there is a feeble detonation. The salt is easily soluble in hot and cold water; and insoluble in 90 per cent. alcohol. The aq. soln. does not decompose when boiled. If warmed with potassium tetrachloroplatinite, not in excess, some $Pt(NH_3)_2(NO_2)_2$, or $[Pt(NH_3)_4]Pt(NO_2)_4$, is formed—**platinous tetramminotetranitritoplatinite**; this compound is also produced by the action of platinous tetramminodichloride on potassium tetranitritoplatinite. L. A. Tschugaeff and W. Chlopin obtained it by the action of platinous tetramminodichloride on the complex salt, $[Pt(C_2H_5.S.C_2H_4.S.C_2H_5)_2]Pt(NO_2)_4$. The yellow six-sided needles can be heated below 250° in dry air without change, but at that temp. they blacken, forming $[Pt(NH_3)_2(NO_2)_2]Pt(NO_2)_2$. The salt is sparingly soluble in cold water, and easily soluble in hot water. Aq. ammonia dissolves it more easily than does water; and after boiling the ammoniacal soln., the cis- and trans-forms of platinous diamminodinitrite are produced. Cold dil. acids have no action; but the salt is decomposed by conc. sulphuric acid; conc. hydrochloric acid acts slowly in the cold, rapidly when heated. L. A. Tschugaeff and S. S. Kiltuinowich prepared **platinous nitritotriamminonitrite,** $[(NH_3)_3Pt(NO_2)](NO_2)$. The tetramminotetranitritoplatinite occurs in the isomeric forms:

$$\left[\begin{matrix}NH_3\\NH_3\end{matrix}\;Pt\;\begin{matrix}NO_2\\NO_2\end{matrix}\right] \qquad\qquad \left[\begin{matrix}NO_2\\NH_3\end{matrix}\;Pt\;\begin{matrix}NH_3\\NO_2\end{matrix}\right]$$

J. Lang heated platinum tetramminodinitrite to 140°–150°, and obtained **platinous trans-diamminodinitrite,** $[Pt(NH_3)_2(NO_2)_2]$; and he also made it by digesting the diiodide with silver nitrite. P. T. Cleve passed the red nitrous fumes from starch and nitric acid into a soln. of the trans-dinitrate; and also boiled the trans-dichloride with potassium nitrite in order to prepare this compound. L. Ramberg purified the product by recrystallization from a hot soln. of sodium nitrite. M. Vèzes made it by the action of ammonia on a soln. of potassium oxalatodinitritoplatinite, and K. A. Hofmann and K. Buchner, by the action of conc. aq. ammonia on $[Pt(C_7H_9N)(NO_2)_3]H.C_7H_9N$. The white crystalline powder contains small four-sided prisms. It is not changed at 100°, but detonates feebly at about 240°. It is sparingly soluble in cold water, and a little more soluble in hot water; L. Ramberg said that 0·63 grm. of the salt is dissolved per litre at 25°. It is insoluble in alcohol. It is more soluble in aq. ammonia than in water without forming the tetramminodinitrite. The salt is decomposed by hot nitric acid, and the soln. gives colourless crystals of the diamminodinitritodinitrate; sulphurous acid is oxidized to sulphuric acid; conc. sulphuric acid decomposes the salt; hydrochloric acid attacks it in the cold; bromine forms an addition product, $Pt(NH_3)_2(NO_2)_2Br_2$. If platinous tetramminotetranitritoplatinite be heated to 230°–240°, **platinous diamminotetranitritoplatinite,** $[Pt(NH_3)_2(NO_2)_2]Pt(NO_2)_2$, is formed. J. Lang obtained the same product by heating silver tetranitritoplatinite with platinous trans-diamminodichloride, extracting with water, and drying over sulphuric acid. The golden yellow scales are not changed at 100°, but they are decomposed at 250°–260°. The salt dissolves sparingly in cold water, readily in hot water. Aq. ammonia dissolves it more readily than does water, and the soln. deposits the cis- and trans-diamminodinitrite on cooling. Cold acids slowly decompose the salt.

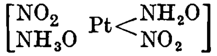
P. T. Cleve prepared **platinous cis-diamminodinitrite,** $[Pt(NH_3)_2(NO_2)_2]$, by the method employed for the trans-salt, using the cis-salts as the initial products. L. Ramberg purified this salt by the same method as that previously employed. The same salt was made by J. Lang as indicated above; and L. Ramberg made it in colourless needles by the action of ammonia on platinous bisethylthiolacetodinitrate. P. T. Cleve said that the boiling soln. deposits pale yellow prisms. The salt detonates when heated, and is sparingly soluble in cold water; L. Ramberg said that a litre of water dissolves 0·88 grm. of the salt at 25°. According to P. T. Cleve, the salt is decomposed by nitric acid, and sulphur dioxide. Aqua regia produces ammonium chloroplatinate; bromine and chlorine furnish cis- and trans-$[Pt(NH_3)_2(NO_2)_2X_2]$; dil. hydrochloric acid scarcely attacks it in the cold, but when heated, the salt is decomposed.

I. I. Tschernyaeff treated platinous oxalatodinitrite with hydroxylamine and obtained **platinous cis-dinitritohydroxylamine,** $[Pt(NH_3O)_2(NO_2)_2]$, which, with ammonia forms **platinous nitritodihydroxylaminoammine,** $[Pt(NH_3O)(NH_2O)(NH_3)(NO_2)]$, or



$$\left[\begin{matrix}NH_3O\\NH_3\end{matrix}\ Pt<\begin{matrix}NH_2O\\NO_2\end{matrix}\right]$$

This compound is not attacked by cold acids, but with hot hydrochloric acid, it forms **platinous nitritochlorohydroxylammine,** $Pt[(NH_3O)N(H_3)(NO_2)Cl]$, which, with water, hydrolyzes to form **platinous hydroxynitritohydroxylaminoammine,** $[Pt(NH_3O)(NH_3)(NO_2)(OH)]$, and forms a monohydrate with alkali-lye, which, with hydrochloric acid, reforms the chloronitrite. Both the hydrate, and the nitritodihydroxylaminoammine with pyridine form **platinous nitritopyridinohydroxylaminoammine,** $[Pt(NH_2O)(Py)(NH_3)(NO_2)]$, which is decomposed by acids. Similarly **platinous trans-dinitritohydroxylamine,** $[Pt(NH_3O)(NH_2O)(NO_2)_2]$, or



$$\left[\begin{matrix}NO_2\\NH_3O\end{matrix}\ Pt<\begin{matrix}NH_2O\\NO_2\end{matrix}\right]$$

is obtained in yellowish needles, less soluble in water than the *cis*-compound, and which, with ammonia, forms $[Pt(NH_3O)_2(NH_3)(NO_2)]$, and, with dil. hydrochloric acid, furnishes **platinous nitritodihydroxylaminoamminochloride,** $[Pt(NH_3O)_2(NH_3)(NO_2)]Cl$; it is re-formed by treating this compound with alkali-lye, and with hydrochloric acid and potassium chloroplatinate dark red crystals of the **chloroplatinite,** $[Pt(NH_3O)_2(NH_3)(NO_2)]_2PtCl_4$, are formed. These compounds illustrate how the substitution of an atom of hydrogen in hydroxylamine increases the acid properties of the latter by the proximity of the NO_2-group; just as in picric acid, the activity of the (OH)-group is augmented by the NO_2-groups.

I. I. Tschernyaeff found that platinous trans-dinitrodiammine with hydroxylamine hydrochloride gives off nitrogen, and forms **platinous trans-chloronitritodiammine,** $[Pt(NH_3)_2Cl(NO_2)]$; and with more hydroxylamine there is formed **platinous trans-nitritohydroxylaminodiamminonitrite,** $[Pt(NH_3)_2(NH_3O)(NO_2)]NO_2$, which gives a red **chloroplatinite**; and similarly with **platinous cis-nitritohydroxylaminodiamminonitrite,** $[Pt(NH_3)_2(NH_3O)(NO_2)]NO_2$, which also forms a dark red chloroplatinite.

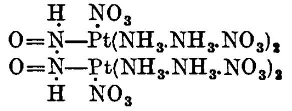
I. I. Tschernyaeff found that an excess of hydroxylamine reacts with platinous trans-pyridinoamminodinitrite to form **platinous trans-nitritohydroxylaminopyridinoamminonitrite,** $[Pt(NH_3O)(Py)(NH_3)(NO_2)]NO_2$, which gives a rose-coloured **chloroplatinite** in rhombic plates. Platinous trans-pyridinoamminodinitrite and ammonia furnish **platinous cis-**

nitritopyridinodiamminonitrite, $[Pt(NH_3)_2(Py)(NO_2)]NO_2$, which gives a yellow **chloroplatinite.** Sodium nitrite acts on platinous trans-hydroxylaminopyridinodichloride, $[Pt(NH_3O)(Py)Cl_2)$, to form **platinous trans-dinitritohydroxylaminopyridine,** $[Pt(NH_3O)(Py)\cdot(NO_2)_2]$; and on platinous trans-hydroxylaminoamminodichloride, $[Pt(NH_3O)(NH_3)Cl_2]$, to form **platinous trans-chloronitritohydroxylaminoammine,** $[Pt(NH_3O(NH_3)Cl(NO_2)]$. The trans-chloronitrites with hydroxylamine hydrochloride yield the trans-dinitrites; and a number of pyridine compounds were prepared, which with alkali-lye form the trans-hydroxynitrites. Thus, the trans-chloronitrite yields needles of **platinous trans-nitritopyridinodiamminochloride,** $[Pt(NH_3)_2Py(NO_2)]Cl$, which forms rose-coloured plates of the **chloroplatinite.** When platinous chloronitritopyridinoammine, $[Pt(NH_3)(Py)Cl(NO_2)]$, is treated with hydroxylamine, it forms colourless needles of **platinous nitritohydroxylaminopyridinoamminochloride,** $[Pt(NH_3O)(NH_3)(Py)(NO_2)]Cl$: when platinous nitritochloropyridinohydroxylamine, $[Pt(NH_3O)(Py)Cl(NO_2)]$, is treated with ammonia, it forms a yellow gelatinous mass which, with hydrochloric acid and potassium chloroplatinite forms bright yellow chloroplatinite, of **platinous nitritohydroxylaminopyridinoammine,** $[Pt(NH_3O)(NH_3)\text{-}(Py)(NO_2)]_2PtCl_4$. If platinous nitritochlorohydroxylaminoammine is treated with pyridine and potassium chloroplatinite, rose-coloured prisms of the chloroplatinite of **platinous nitritohydroxylaminopyridinoammine,** $[Pt(NH_3O)NH_3)(Py)(NO_2)]_2PtCl_4.2H_2O$ are formed.

I. I. Tschernyaeff showed that if platinous trans-dinitritodiammine is treated with hydrazine sulphate it forms **diplatinous dinitritodihydrazinodiamminosulphate,** $[(NH_3)(NO_2)Pt(N_2H_4)_2Pt(NH_3)(NO_2)]SO_4$; and with platinous trans-dinitritohydroxylaminoammine, **diplatinous dinitritodihydroxylaminodihydrazinosulphate,** $(NH_3O)(NO_2)Pt(N_2H_4)_2Pt(NH_3)(NO_2)]SO_4$, is formed. Platinous cis- and trans-dinitrodiammines with ethylenediamine respectively form **platinous dinitroethylenediamine,** $[Pt(en)(NO_2)_2]$, and **platinous nitritoamminodiethylenediaminohydroxide,** $[Pt(en)_2(NH_3)(NO_2)]OH$; while platinous trans-nitritochlorodiammine gives **platinous dinitritoethylenediaminotetramminochloride,** $[(NH_3)_2(NO_2)Pt(en)Pt(NO_2)(NH_3)_2]Cl_2$, which forms a bright yellow **chloroplatinite**; and when it is boiled with ethylenediamine and treated with potassium chloroplatinite, it yields the chloroplatinite of **platinous nitritoamminodiethylenediamine.** If platinous nitritochloro-hydroxylaminoammine is treated with ethylenediamine, it furnishes the chloroplatinite of **diplatinous dinitritodihydroxylaminoethylenediaminodiammine,** $[(NH_3O)(NH_3)(NO_2)Pt(en)Pt(NO_2)(NH_3)(NH_3O)].PtCl_4$.

E. Koefoed prepared a series of salts with *dimethylamine* in place of ammonia, $[Pt\{(CH_3)_2NH\}_2(NO_2)_2]$; S. G. Hedin, *pyridine*, cis- and trans-$[Pt(C_5H_5N)_2(NO_2)_2]$; L. Tschugaeff and W. Chlopin, C. W. Blomstrand, and C. Enebuske, *dimethyl sulphide*, trans-$[Pt\{(CH_3)_2S\}_2(NO_2)_2]$; C. W. Blomstrand, and M. Weibull, *diethyl sulphide*, trans-$[Pt\{(C_2H_5)_2S\}_2(NO_2)_2]$; C. Rudelius, and C. W. Blomstrand, *dipropyl sulphide*, cis- and trans-$[Pt\{(C_3H_7)_2S\}_2(NO_2)_2]$; C. Rudelius, and M. Weibull, *diisopropyl sulphide*, trans-$[Pt\{(C_3H_7)_2S\}_2(NO_2)_2]$; H. Löndahl, and M. Weibull, *dibutyl sulphide*, cis- and trans-$[Pt\{(C_4H_9)_2S\}_2(NO_2)_2]$; H. Löndahl, and C. W. Blomstrand, *dibenzylsulphide*, $[Pt\{(C_6H_5.CH_2)_2S\}_2(NO_2)_2]$; H. Löndahl, *diethylene sulphide*, $[Pt(C_2H_4)_2S_2(NO_2)_2]$; L. Tschugaeff and W. Chlopin, *dimethylethylenedithioether*, $[Pt(CH_3.S.C_2H_4.S.CH_3)_2(NO_2)_2]$, *diethylethylenedithioether*, $[Pt(C_2H_5.S.C_2H_4.S.C_2H_5)_2(NO_2)_2]$; *dipropylethylenedithioether*, $[Pt(C_3H_7.S.C_2H_4.S.C_3H_7)_2(NO_2)_2]$, *dibutylethylenedithioether*, $[Pt(C_4H_9.S.C_2H_4.S.C_4H_9)_2\cdot(NO_2)_2]$, *diethylpropylenedithioether*, $[Pt(C_2H_5.S.C_3H_6.S.C_2H_5)_2(NO_2)_2]$, *diethylhydroxypropylenedithioether*, $[Pt(C_2H_5.S.CH(OH).CH_2.S.C_2H_5)_2(NO_2)_2]$; and the salt $[Pt\{(C_2H_5)_2S\}\{(C_3H_7)_2S\}(NO_2)_2]$; S. Tyden, *thioglycollic acid*, $[Pt\{S(CH_2.COOH)_2\}_2(NO_2)_2]$, *sodium thioglycollate*, $[Pt\{S(CH_2.COONa)_2\}_2(NO_2)_2]$, and $[Pt\{S(CH_2.COOH)_2\}\cdot(HOOC.CH_2S.CH_2COOH)(NO_2)]$; J. Petrén, *diethylselenide*, $[Pt\{(C_2H_5)_2Se\}_2(NO_2)_2]$; and $[Pt\{(C_2H_5)_2S\}\{(C_2H_5)_2Se\}(NO_2)_2]$; K. A. Hofmann and K. Buchner, *toluidine*, $[Pt(C_7H_9N)(NO_2)_3]H.C_7H_9N$.

O. Carlgren and P. T. Cleve prepared **platinum dihydroxytetrammine nitrite,** $[Pt(NH_3)_4(OH)_2](NO_2)_2$, in acicular crystals by the action of silver nitrite on the chloride. P. T. Cleve, and W. Odling prepared **platinum dinitritotetrammine nitrate,** $[Pt(NH_3)_4(NO_2)_2](NO_3)_2$, by passing the red vapours from starch and nitric acid into an aq. soln. of platinous tetramminosulphate; E. A. Hadow, and B. Gerdes, by passing these vapours into a soln. of platinous tetramminonitrate acidified with nitric acid; E. Koefoed, by the action of sodium nitrite on the same soln. According to P. T. Cleve, B. Gerdes, and E. A. Hadow, the deep blue powder consists of microscopic octahedra or dodecahedra. E. A. Hadow said that the salt can be dried at 100° without decomposition ; and P. T. Cleve observed no change at 120°, but at 140° it becomes yellow and then brown. At 143°, the salt decomposes ; and at 170°, E. Koefoed found that it suddenly explodes. It dissolves in water with decomposition, and when the aq. soln. is crystallized, $[Pt(NH_3)_4(OH)(NO_3)](NO_3)_2$ is formed. It dissolves in soda-lye with decomposition. E. A. Hadow represented the constitution :



$$\begin{array}{l} \;\;\;\mathrm{H}\;\;\;\mathrm{NO_3} \\ \mathrm{O{=}\dot{N}{-}\dot{P}t(NH_3.NH_3.NO_3)_2} \\ \mathrm{O{=}\dot{N}{-}\dot{P}t(NH_3.NH_3.NO_3)_2} \\ \;\;\;\mathrm{H}\;\;\;\mathrm{NO_3} \end{array}$$

P. T. Cleve made *platinum nitritoiodo-tetrammine nitrate*, $[Pt(NH_3)_4(NO_2)I](NO_3)_2$; *platinum nitritotrichlorodiammine*, $[Pt(NH_3)_2Cl_3(NO_2)]$; *platinum cisdinitritodinitratodiammine*, $[Pt(NH_3)_2(NO_2)_2(NO_3)_2]$; P. T. Cleve, and C. W. Blomstrand, *platinum cis- and trans-dinitritodichlorodiammine*, $[Pt(NH_3)_2Cl_2(NO_2)_2]$; and *platinum cis- and trans-dinitritodibromodiammine*, $[Pt(NH_3)_2Br_2(NO_2)_2]$; C. W. Blomstrand, *platinum cis-dinitritosulphatodiammine*, $[Pt(NH_3)_2(NO_2)_2(SO_4)]$; P. T. Cleve, *platinum dinitritohydroxychlorodiammine*, $[Pt(NH_3)_2(NO_2)_2(OH)Cl]$; and *platinum dinitritonitratochlorodiammine*, $[Pt(NH_3)_2(NO_2)_2(NO_3)Cl]$. J. Petrén, *platinum dinitritodichlorobisdimethylselenide*, $[Pt\{(CH_3)_2Se\}_2(NO_2)_2Cl_2]$; *platinum dinitritodibromobisdimethylselenide*, $[Pt\{(CH_3)_2Se\}_2(NO_2)_2Br_2]$; and *platinum dinitritodiiodobisdimethylselenide*, $[Pt\{(CH_3)_2Se\}_2(NO_2)_2I_2]$; J. Pretrén also prepared *platinum dinitritodibromotetraethylsulphoselenide*, $[Pt\{(C_2H_5)_2Se\{(C_2H_5)_2S\}(NO_2)_2Br_2]$, as well as *platinum dinitritodiiodotetraethylsulphoselenide*. E. Koefoed prepared a complex *platinum nitritonitrosylchlorodiammine hydrochloride*, $Pt(NH_3)_2(NO_2)(NO)Cl.HCl.\frac{3}{4}H_2O$.

L. F. Nilson prepared **dihydrated ammonium tetranitritoplatinite**, $(NH_4)_2Pt(NO_2)_4.2H_2O$, by rubbing together eq. proportions of ammonium chloride and silver tetranitritoplatinite with as little water as possible, and evaporating the soln. in vacuo. The colourless or pale yellow six-sided plates are stable in air. According to H. Töpsöe, the rhombic crystals have the axial ratios $a:b:c=0.4910:1:0.9094$. L. F. Nilson said that the crystals become anhydrous **ammonium tetranitritoplatinite**, $(NH_4)_2Pt(NO_2)_4$, in vacuo over sulphuric acid. If heated over a free flame, the salt explodes. It is sparingly soluble in water. J. Lang reported a *monohydrate* to be formed during the evap. of the aq. soln., but L. F. Nilson could not find it. J. Lang prepared **potassium nitritoplatinite**, or *potassium platinous tetranitrite*, $K_2Pt(NO_2)_4$, by crystallization from a mixture of potassium chloroplatinite and potassium nitrite in the molar proportions 1 : 4. M. Vèzes obtained it from a soln. of platinum in aqua regia and potassium nitrite ; and also from potassium oxalatoplatinite and potassium nitrite. The colourless four- or six-sided monoclinic prisms have, according to H. Töpsöe, the axial ratios $a:b:c=0.6068:1:0.7186$, and $\beta=96°\ 12\frac{1}{2}'$. According to J. Lang, 100 parts of water at 15° dissolve 3·7 parts of the salt, and the solubility is greater in warm water. The soln. has a neutral reaction, and the aq. soln. deposits crystals of the salt undecomposed. J. Lang, L. F. Nilson, M. Vèzes, and H. G. Söderbaum obtained colourless rhombohedra of **dihydrated potassium tetranitritoplatinite**, $K_2Pt(NO_2)_4.2H_2O$, by the slow evaporation of the aq. soln. H. Dufet found the triclinic pinacoids have the axial ratios $a:b:c=0.7282:1:0.7112$, $\alpha=79°\ 50'$, $\beta=108°\ 48'$, and $\gamma=94°\ 50.5'$. The crystals lose nearly all their water in 24 hrs. C. W. Blomstrand observed that chlorine and bromine react with potassium tetranitritoplatinite, forming chloro- or bromo-nitrites ; but iodine has scarcely any action. M. Vèzes prepared a series of chloronitrites, bromonitrites, or iodonitrites, by the action of the halogen or halide acid. J. Lang found that potash-lye decomposes the salt ; alkali carbonates have no action on the salt ; hydrogen sulphide, and ammonium sulphide darken the heated salt ; sulphuric acid or hydrochloric acid makes the soln. dark green ; when the soln. is heated, red fumes are given off ; stannous chloride gives a yellow precipitate and a dark red soln. ; mercurous nitrate gives a white precipitate ; ferrous sulphate, a yellowish-brown precipitate in about 24 hrs. ; urea gives, when heated, a yellow soln. with the evolution of a little gas; urea nitrate acts similarly, and later gives a yellow precipitate which detonates when heated. A. Miolati found that the dry salt with liquid nitrogen peroxide forms a green solid, **potassium dinitroxyltetranitritoplatinite,** $K_2Pt(NO_2)_4.N_2O_4$, which is stable over calcium chloride; but is decomposed over sulphuric acid. It is decomposed at 150°; it is decomposed by aq. ammonia, forming platinous diamminodinitrite; and it forms a complex salt with pyridine, $Pt(C_2H_5N)_2(NO_2)_2$.

L. F. Nilson prepared **rubidium tetranitritoplatinite,** $Rb_2Pt(NO_2)_4$, from the soln. obtained by mixing the silver salt with rubidium chloride. The spontaneous evaporation of the soln. furnishes colourless prisms of **dihydrated rubidium tetranitritoplatinite,** $Rb_2Pt(NO_2)_4.2H_2O$; at 100°, this salt becomes anhydrous. H. Töpsöe found the monoclinic prisms of the anhydrous salt have the axial ratios $a:b:c=0{\cdot}6142:1:0{\cdot}7103$, and $\beta=95°\ 01'$; and they are isomorphous with the potassium salt; the axial ratios of the monoclinic prisms of the dihydrate are $a:b:c=2{\cdot}0109:1:1{\cdot}7935$, and $\beta=91°\ 40'$, and they are isomorphous with the ammonium salt. H. A. Miers emphasized that rubidium does not here occupy an intermediate position crystallographically between potassium and cæsium. L. F. Nilson added that the hydrate is stable in air at ordinary temp., but in a dry atm. efflorescence occurs. The water is lost at 100°. Both salts are soluble in cold water, more so in hot water. L. F. Nilson likewise prepared colourless or pale yellow crystals of **cæsium tetranitritoplatinite,** $Cs_2Pt(NO_2)_4$. The properties are like those of the rubidium salt. H. Töpsöe gave $a:b:c=1{\cdot}6122:1:0{\cdot}6291$, and $\beta=99°\ 50'$ for the axial ratios of the monoclinic prisms. L. F. Nilson prepared colourless prisms of trihydrated **lithium tetranitritoplatinite,** $Li_2Pt(NO_2)_4.3H_2O$, as in the case of the rubidium salt. The water is expelled at 100°; the crystals are hygroscopic, and easily soluble in water. H. Töpsöe found the axial ratios of the rhombic bipyramids to be $a:b:c=0{\cdot}9576:1:0{\cdot}7504$. J. Lang made **sodium tetranitritoplatinite,** $Na_2Pt(NO_2)_4$, by evaporating the soln. obtained by mixing sodium nitrite and sodium tetrachloroplatinite; M. Vèzes, by mixing soln. of hydrochloroplatinic acid and an excess of sodium nitrite; and L. F. Nilson, from mixed soln. of sodium chloride and silver tetranitritoplatinite. The slow evaporation of the soln. furnishes pale yellow, rhombic or monoclinic prisms, which H. Töpsöe found to have the axial ratios $a:b:c=1{\cdot}4442:1:0{\cdot}6637$. The crystals separating from the aq. soln. are probably hydrated, but they readily effloresce. All the water is expelled at 100°. J. Lang said that the salt is very soluble in cold or hot water, and the soln. has a neutral reaction. Chlorine or hydrochloric acid decomposes the soln.

L. F. Nilson treated a conc. soln. of barium tetranitritoplatinite with one of copper sulphate, and obtained acicular, yellow crystals of **copper oxytetranitritoplatinite,** $CuO.3CuPt(NO_2)_4.18H_2O$, which decompose at 100°, and in aq. soln. The mother-liquor from the basic salt furnishes green needles of trihydrated **copper tetranitritoplatinite,** $CuPt(NO_2)_4.3H_2O$, which are decomposed at 100°. The salt is very soluble in water. J. Lang made silver tetranitritoplatinite, $Ag_2Pt(NO_2)_4$, mixing potassium tetranitritoplatinite and silver nitrate in hot conc. soln. and cooling; and E. Priwoznik, by digesting an excess of a silver platinum alloy with nitric acid. The salt can be purified by recrystallization from hot water, and dried at 100°. The yellowish-green, or bronze-yellow, needle-like crystals were found by H. Töpsöe to be monoclinic prisms, with the axial ratios $a:b:c=0{\cdot}9660:1:0{\cdot}5091$, and $\beta=98°\ 0{\cdot}5'$; F. von Foullon gave $a:b:c=0{\cdot}9686:1:0{\cdot}5127$, and $\beta=78°\ 18\frac{1}{2}'$, where 78° is probably a slip of the pen for 98°. The crystals are stable in air. J. Lang said that they blacken when exposed to light, and decompose without detonation when heated; E. Priwoznik observed that nitrogen peroxide is first evolved and then oxygen. The salt is scarcely soluble in cold water, but is readily dissolved by hot water; F. L. Nilson found that small quantities of a basic salt—$Ag_2Pt_2O(NO_2)_2$, silver oxydinitritodiplatinite—are formed when the normal salt is crystallized. The crystals of the basic salt are green or greenish-yellow, four-sided prisms. J. Lang found that ammonia transforms the tetranitrito-platinite into a white substance easily soluble in water, and forming prisms when the aq. soln. is crystallized. Green silver chloride is formed by treating the aq. soln. with hydrochloric acid—the green colour is due to absorbed nitrogen peroxide.

L. F. Nilson prepared **calcium tetranitritoplatinite,** $CaPt(NO_2)_4.5H_2O$, in yellow four-sided prisms by the action of conc. soln. of calcium chloride on the silver salt. The crystals are stable in moist air, but effloresce over sulphuric acid; they lose all their water at 100°; and are very soluble in water. L. F. Nilson prepared **strontium tetranitritoplatinite,** $SrPt(NO_2)_4.3H_2O$, by the action of a soln. of strontium chloride on the silver salt. The colourless or pale yellow, six-sided plates were shown by H. Töpsöe to be triclinic pinacoids—pseudomonoclinic—with axial ratios $a:b:c=0{\cdot}5598:1{\cdot}5712$, or $\alpha=93°\ 6'$, $\beta=90°\ 0'$, and $\gamma=90°\ 0'$. L. F. Nilson added that the crystals are stable in air, and lose two-thirds the total water at 100°; they blacken at dull redness; and are sparingly soluble in cold water, but readily soluble in hot water. J. Lang, and L. F. Nilson made **barium tetranitritoplatinite,** $BaPt(NO_2)_4.3H_2O$, by the action of soln. of barium chloride on the silver salt. The colourless plates or prisms were found by H. Töpsöe to be triclinic pinacoids—pseudomonoclinic—with axial ratios $a:b:c=0{\cdot}5722:1:1{\cdot}7172$, and $\alpha=92°\ 12'$, $\beta=90°\ 0'$, and $\gamma=90°\ 0'$. J. Lang, and L. F. Nilson found the crystals to be quite stable in air; and after drying in air, to lose nothing in weight in vacuo over potassium hydroxide. The crystals are sparingly soluble in cold water, but readily soluble in hot water. They are also more soluble in cold water than the potassium salt.

L. F. Nilson prepared a basic salt—**beryllium oxytetranitritodiplatinite,** $BePt_2O(NO_2)_4.9H_2O$—from conc. soln. of beryllium sulphate and barium tetranitritoplatinite, after evaporation first on a water-bath and then over conc. sulphuric acid or in vacuo. The small red pyramidal crystals lose six mols of water at 100°; they are sparingly soluble in cold water, forming a yellow soln. which develops nitrous fumes on a water-bath. L. F. Nilson obtained **magnesium tetranitritoplatinite,** $MgPt(NO_2)_4.5H_2O$, by the action of magnesium sulphate on the barium salt. The colourless six-sided prisms are monoclinic, and H. Töpsöe found for the axial ratios $a:b:c=0{\cdot}6101:1:0{\cdot}4101$, and $\beta=98°\ 35{\cdot}5'$. L. F. Nilson found the crystals to be stable at 100°, and to decompose at dull redness. L. F. Nilson obtained colourless or pale yellow crystals of **zinc tetranitritoplatinite,** $ZnPt(NO_2)_4.8H_2O$, from zinc sulphate and the barium salt. They are fairly stable in air, but decompose at 100°. They are readily soluble in water. H. Töpsöe said that the triclinic pinacoids are isomorphous with the nickel and manganese salts. L. F. Nilson made yellow crystals of **cadmium tetranitritoplatinite,** $CdPt(NO_2)_4.3H_2O$, from cadmium sulphate and the barium salt. They are stable in moist air; effloresce in dry air, and lose all their water of crystallization without decomposition at 100°. H. Töpsöe said the monoclinic prisms have the axial ratios $a:b:c=1{\cdot}0627:1:1{\cdot}5850$, and $\beta=98°\ 25{\cdot}5'$. L. F. Nilson, and J. Lang obtained a basic salt—**mercurous oxytetranitritoplatinite,** $Hg_2O.Hg_2Pt(NO_2)_4.H_2O$—by the action of a feebly acid soln. of mercurous nitrate on a soln. of potassium tetranitritoplatinite. The pale yellow precipitate consists of microscopic prisms; they lose a mol of water at 60°; and blacken at 100°. L. F. Nilson said that if boiling soln. of mercuric chloride and silver tetranitritoplatinite are mixed, silver chloride is precipitated, and the filtrate when evaporated gives a yellow amorphous substance and pale yellow crystals which could not be separated—one may be normal or basic *mercuric tetranitritoplatinite.*

L. F. Nilson evaporated over sulphuric acid the liquid obtained by the action of barium tetranitritoplatinite on aluminium sulphate. The colourless cubic crystals of **aluminium dodecanitritotriplatinate,** $Al_2Pt_3(NO_2)_{12}.14H_2O$, so obtained are fairly stable, but decompose at 100°; if the aq. soln. be evaporated on a water-bath orange-red needles are produced with the composition $AlPt_2(OH)_3(NO_2)_4.4H_2O$, **aluminium trihydroxytetranitritodiplatinite.** They lose water at 100°; and are slightly soluble in cold water; easily soluble in water; and soluble in alcohol. By treating soln. of the silver salt with indium trichloride, and evaporating the filtrate, L. F. Nilson obtained red, needle-like crystals of a basic salt—**indium trihydroxytetranitritoplatinite,** $InPt_2(OH)_3(NO_2)_4.4H_2O$—sparingly soluble in cold water. L. F. Nilson also prepared lemon-yellow, four-sided prisms of **yttrium dodecanitritotriplatinite,** $Y_2[4NO_2.Pt]_3.9H_2O$, and $Y_2[4NO_2.Pt]_3.21H_2O$; orange-yellow, four-sided prisms of **erbium dodecanitritotriplatinite,** $Er_2[4NO_2.Pt]_3.9H_2O$, and $Er_2[4NO_2.Pt]_3.21H_2O$; yellow, four-sided plates or rhombohedra of **cerous dodecanitritotriplatinite,** $Ce_2[4NO_2.Pt]_3.18H_2O$; yellow, four-sided plates of rhombohedra of **lanthanum dodecanitritotriplatinite,** $La_2[4NO_2.Pt]_3.18H_2O$; and yellow, four-sided plates or rhombohedra **didymium dodecanitritotriplatinite,** $Di_2[4NO_2.Pt]_3.18H_2O$, from the barium salt and the sulphate of the rare earth. Colourless four- or six-sided needles or prisms of **thallous tetranitritoplatinite,** $Tl_2Pt(NO_2)_4$, were also made by the action of thallous sulphate on the barium salt. The crystals are stable in moist and dry air, and at 100°; they are soluble in cold water, more so in hot water. H. Töpsöe gave for the axial ratios of the monoclinic prisms $a:b:c=1·2309:1:0·9034$, and $\beta=105° 30'$. L. F. Nilson prepared **lead tetranitritoplatinite,** $PbPt(NO_2)_4.3H_2O$, from the filtrate by treating soln. of lead chloride and silver tetranitritoplatinite. The six-sided prisms are stable in air; lose their water at 100°; and are sparingly soluble in water. H. Töpsöe gave for the monoclinic prisms—pseudohexagonal—the axial ratios $a:b:c=0·5471:1:1·3055$, and $\alpha=92° 18'$.

L. F. Nilson prepared crystals of **chromium trihydroxytetranitritodiplatinite,** $CrPt_2(OH)_3(NO_2)_4.11H_2O$, from the soln. obtained by treating soln. of chromic sulphate with barium tetranitritoplatinite. The small red crystals resemble the basic beryllium salt. They lose nine mols of water at 100°; and are soluble in water. He also obtained **manganese tetranitritoplatinite,** $MnPt(NO_2)_4.8H_2O$, from manganese sulphate and the barium salt. The crystals are fairly stable in air, but gradually form brown manganese oxide; they decompose at 100°. H. Töpsöe gave for the axial ratios of the triclinic pinacoids, $a:b:c=0·7025:1:—$, and $\alpha=84° 31'$, $\beta=107° 52'$, and $\gamma=98° 43'$. By evaporating in vacuo over sulphuric acid the filtrate from a mixed soln. of ferrous sulphate and the barium salt, L. F. Nilson obtained a basic salt—**ferrous trioxydodecanitritohexaplatinite,** $Fe_2Pt_6O_3(NO_2)_{12}.30H_2O$; and similarly by evaporating the filtrate from a mixture of ferric chloride and silver tetranitritoplatinite. The crystals resemble those of the basic salts of beryllium and chromium. They lose 24 mols of water at 100°, and are soluble in water. He also prepared **cobaltous tetranitritoplatinite,** $CoPt(NO_2)_4.8H_2O$, by evaporating the filtrate from a soln. of cobalt sulphate and the barium salt. The red, four-sided prisms are isomorphous with those of the manganese salt. The crystals are stable in air; decompose at 100°; and dissolve readily in water. H. Töpsöe found the axial ratios of the triclinic pinacoids to be $a:b:c=0·6998:1:0·88$, and $\alpha=84° 57'$, $\beta=108° 5'$, and $\gamma=97° 0'$. The corresponding **nickel tetranitritoplatinite,** $NiPt(NO_2)_4.8H_2O$, was obtained by L. F. Nilson, in a manner similar to that used for the cobalt salt. The properties are similar, and H. Töpsöe found the crystals to be isomorphous.

A. Miolati obtained **potassium hydrochlorotetranitritoplatinite,** $K_2Pt(NO_2)_4.HCl$, by treating powdered potassium tetranitritoplatinite with cold, conc. hydrochloric acid. The product is soluble in water, and on evaporation crystals of **potassium chlorotrinitritoplatinite,** $K_2Pt(NO_2)_3.2H_2O$, are formed. M. Vèzes made the latter salt by heating a soln. of a mol of potassium tetranitritoplatinite, and a mol of hydrogen chloride in dil. soln. The pale yellow plates are stable in air; lose water at 100°; and melt at a higher temp., giving off nitrous fumes. 100 parts of cold water dissolve 33·3 parts of salt; and hot water, 50 parts. The yellow soln. is stable even at 100°. A soln. of potassium nitrite reforms the tetranitritoplatinite, and an excess of chlorine forms chloroplatinate; a little chlorine-water forms trichlorotrinitritoplatinate; and a little hydrogen chloride forms

potassium dichlorodinitritoplatinite, $K_2Pt(NO_2)_2Cl_2$. The latter salt was also made by M. Vèzes by cooling a mixed conc. soln. of potassium tetrachloroplatinite and tetranitritoplatinite; and by boiling equi-molar parts of potassium oxalatodinitritoplatinite, and copper chloride. The yellow needles were shown by H. Dufet to be monoclinic prisms with axial ratios $a:b:c=0\cdot5538:1:0\cdot3074$, and $\beta=103^\circ 51'$. The crystals are stable in air; they lose no weight at 100°; they melt and decompose at dull redness; 100 parts of cold water dissolve 33·3 parts of salt, and hot water, 50 parts. The aq. soln. is very stable. An excess of chlorine or hydrochloric acid converts it into chloroplatinate, and an excess of potassium nitrite into nitritoplatinite. A. Miolati was unable to prepare potassium dichlorodinitritoplatinite, $K_2PtCl_2(NO_2)_2$.

M. Vèzes prepared **potassium bromotrinitritoplatinite,** $K_2Pt(NO_2)_3Br.2H_2O$, as in the case of the corresponding chloro-salt. The crystals are isomorphous with the same compound. The properties are also analogous. M. Vèzes made **potassium dibromodinitritoplatinite,** $K_2Pt(NO_2)_2Br_2.H_2O$, by the methods employed for the corresponding chloro-salt. The pale yellow plates are triclinic pinacoids which H. Dufet found to have the axial ratios $a:b:c=0\cdot9920:1:1\cdot3170$, and $\alpha=90^\circ 58'$, $\beta=91^\circ 42\cdot5'$, and $\gamma=91^\circ 7'$. The properties of the salt resemble those of the corresponding chloro-salt. L. F. Nilson prepared **potassium diiododinitritoplatinite,** $K_2Pt(NO_2)_2I_2.2H_2O$, by the action of a mol of potassium tetranitritoplatinite on 2 gram-atoms of iodine in alcoholic soln. at 30°–40°; and M. Vèzes, by the action of eq. proportions of lead iodide and potassium oxalatodinitritoplatinite. The conc. of the soln. furnishes reddish-yellow prisms which H. Dufet classed as tetragonal bipyramids with the axial ratio $a:c=1:0\cdot5891$; the refractive indices for Na-light are $\omega=1\cdot7909$, and $\epsilon=1\cdot6527$; the optical character is negative. The dichroic crystals are pale greenish-yellow viewed parallel to the c-axis; and orange, perpendicular to that axis. L. F. Nilson found that the crystals are stable in air; they lose their water at 100°; they are very soluble in water; the aq. soln. darkens at 100°; the salt is very soluble in alcohol. L. F. Nilson made **rubidium diiododinitritoplatinite,** $Rb_2Pt(NO_2)_2I_2.2H_2O$, from a soln. of rubidium sulphate and barium diiodonitritoplatinite. The lemon-yellow plates were considered by P. Groth to be triclinic pinacoids, and to have the axial ratios $a:b:c=0\cdot9418:1:0\cdot5873$, and $\alpha=84^\circ 41'$, $\beta=98^\circ 20'$, and $\gamma=87^\circ 24'$. H. A. Miers emphasized that rubidium is not always intermediate between potassium and cæsium crystallographically, as here. G. Negri considers these observations are not accurate. The salt is stable in air; it loses its water at 100°; and is readily dissolved by water. L. F. Nilson prepared the corresponding **cæsium diiododinitritoplatinite,** $CsPt(NO_2)I_2{\cdot}2H_2O$, in a similar manner. The properties are also similar. The lemon-yellow, monoclinic, prismatic crystals were found by P. Groth to have the axial ratio $a:b:c=0\cdot9425:0\cdot6502$, and $\beta=98^\circ 20'$. L. F. Nilson prepared yellow crystals of **lithium diiododinitritoplatinite,** $Li_2Pt(NO_2)_2I_2.6H_2O$, in a similar manner. They deliquesce in air; lose 5 mols of water at 100°, and decompose; they are very soluble in water. L. F. Nilson also made **sodium diiododinitritoplatinite,** $Na_2Pt(NO_2)_2I_2.4H_2O$, in a similar way. The lemon-yellow crystals are stable in air; lose all their water at 100°; and are very soluble in water. P. Groth found the axial ratios of the triclinic pinacoids to be $a:b:c=0\cdot9049:1:0\cdot7126$, and $\alpha=102^\circ 9'$, $\beta=111^\circ 23\cdot5'$, and $\gamma=80^\circ 31\cdot5'$. They are feebly dichroic. The corresponding **cupric diiododinitritoplatinite,** or a basic derivative, was obtained by L. F. Nilson by the action of cupric sulphate on the barium salt. Green, four-sided, prismatic crystals were mixed with a black substance. L. F. Nilson prepared **silver diiododinitritoplatinite,** $Ag_2Pt(NO_2)_2I_2$, by the action of silver nitrate on an alkali diiododinitritoplatinite. The lemon-yellow powder is amorphous and it is decomposed by water: $2Ag_2Pt(NO_2)_2I_2+H_2O=4AgI+PtO.H_2Pt(NO_2)_4$. The salt decomposes at 100°, and it is very sparingly soluble in water. L. F. Nilson prepared **calcium diiododinitritoplatinite,** $CaPt(NO_2)I_2.6H_2O$, by the action of alcoholic iodine on calcium tetranitritoplatinite. The yellowish-red monoclinic prisms were found by P. Groth to have the axial ratios $a:b:c=1{\cdot}238:1:1{\cdot}794$, and $\beta=124°\ 14'$. The crystals are stable in air; give off 5 mols of water at 100° with decomposition; and are very soluble in water. L. F. Nilson also made **strontium diiododinitritoplatinite**, $SrPt(NO_2)_2I_2.8H_2O$, in a similar way. The amber-yellow plates are stable in air, but they become matte; they lose 6 mols of water at 100°; and are very soluble in water. P. Groth found the monoclinic prisms have the axial ratios $a:b:c=0{\cdot}9175:1:1{\cdot}8101$, and $\beta=119°\ 3'$; the optic axial angle $2E=80°–90°$. L. F. Nilson also made **barium diiododinitritoplatinite**, $BaPt(NO_2)_2I_2.4H_2O$, by the method used for the calcium salt. The amber-yellow crystals are stable in air; give off a mol of water at 100°; and are very soluble in water. P. Groth gave $a:b:c=0{\cdot}8456:1:0{\cdot}5435$, and $\beta=112°\ 4\frac{1}{2}'$ for the axial ratios of the monoclinic prisms; and $2E=c.\ 75°$ for the optic axial angle.

L. F. Nilson made **beryllium diiododinitritoplatinite**, $BePt(NO_2)_2I_2.6H_2O$, from beryllium sulphate and the barium salt—the original represents beryllia-like alumina. The yellow four-sided plates smell of iodine; they are decomposed at 100°; and are readily soluble in water. He also made **magnesium diiododinitritoplatinite**, $MgPt(NO_2)_2I_2.8H_2O$, in a similar manner. The yellow tabular crystals are stable in moist air, but effloresce in dry air; they lose water and decompose at 100°; and are readily dissolved by water. The aq. soln. is partially decomposed on a water-bath. P. Groth gave $a:b:c=0{\cdot}4890:1:0{\cdot}3724$, and $\beta=99°\ 29'$ for the axial ratios of the monoclinic prisms. L. F. Nilson prepared **zinc diiododinitritoplatinite**, $ZnPt(NO_2)_2I_2.8H_2O$, in the form of greenish-yellow, small, four-sided columns. The properties are like those of the magnesium salt. Yellow prismatic crystals of **cadmium diiododinitritoplatinite**, $CdPt(NO_2)_2I_2.2H_2O$, were made in a similar way. They are stable in air and at 100°, and are very soluble in water. He also obtained a dark brown, imperfectly crystallized mass of **mercurous oxydiiododinitritoplatinite**, $Hg_2O.2Hg_2Pt(NO_2)_2I_2.9H_2O$, by the action of mercurous nitrate on the barium salt. He could not procure **mercuric diiododinitritoplatinite** by the action of mercuric chloride on the barium salt.

L. F. Nilson made **aluminium hexaiodohexanitritotriplatinite**, $Al_2Pt_3(NO_2)_6I_6.27H_2O$, by the action of aluminium sulphate on the barium salt, and evaporating the soln. at ordinary temp. The yellow needles have properties like those of the beryllium salt. Thallous sulphate and the sodium salt give small yellow crystals of **thallous diiododinitritoplatinite**, $Tl_2Pt(NO_2)_2I_2$, which are stable in air and at 100°. The following salts were also made from the barium salt and the corresponding sulphate: yellowish-green crystals of **yttrium hexaiodohexanitritotriplatinite**, $Y_2Pt_3(NO_2)_6I_6.27H_2O$; **erbium hexaiodohexanitritotriplatinite**, $Er_2Pt_3I_6(NO_2)_6.18H_2O$; **cerous hexaiodohexanitritotriplatinite**, $Ce_2Pt_3I_6(NO_2)_6.18H_2O$; **lanthanum hexaiodohexanitritotriplatinite**, $La_2Pt_3I_6(NO_2)_6.24H_2O$; and **didymium hexaiodohexanitritotriplatinite**, $Di_2Pt_3I_6(NO_2)_6.24H_2O$. Lead nitrite and the barium salt furnish **lead dihydroxydiiododinitritoplatinite**, $Pb(OH)_2.PbPt(NO_2)I_2$, in yellow microscopic crystals, stable in air and at 100°; and soluble in water. Manganese sulphate and the barium salt furnish yellow six-sided plates of **manganese diiododinitritoplatinite**, $MnPt(NO_2)_2I_2.8H_2O$; they are very slowly decomposed in air; easily decomposed at 100°; soluble in water without decomposition; and the aq. soln. can be conc. on a water-bath with very little decomposition. With ferrous sulphate and the barium salt, **ferrous diiododinitritoplatinite**, $FePt(NO_2)_2I_2.8H_2O$, is obtained in small, yellow, four-sided prisms, which are decomposed only very slowly in air, but quickly at 100°. With ferric sulphate and the barium salt, yellowish-green needles of **ferric hexaiodohexanitritotriplatinite**, $Fe_2Pt_3(NO_2)_6I_6.6H_2O$, are formed. They smell of iodine; decompose at 100°; and are soluble in water. L. F. Nilson prepared **cobalt diiododinitritoplatinite**, $CoPt(NO_2)_2I_2.8H_2O$, in an analogous manner. It forms yellow plates which slowly decompose in air, and decompose rapidly at 100°. Green plates of **nickel diiododinitritoplatinite**, $NiPt(NO_2)_2I_2.8H_2O$, were similarly prepared. This salt is very like the cobalt salt. C. W. Blomstrand, A. Miolati and I. Bellucci, and M. Vèzes passed chlorine into an aq. soln. of potassium tetranitritoplatinite, and obtained pale yellow prisms of **potassium dichlorotetranitritoplatinate,** $K_2PtCl_2(NO_2)_4$. The monoclinic prismatic crystals were found by H. Dufet to have the axial ratios $a:b:c=1{\cdot}021:1:1{\cdot}322$, and $\beta=102°\ 16'$. M. Vèzes found that the crystals are not changed in air; they lose no water at 100°; and melt with decomposition at dull redness. 100 parts of cold water dissolve 2·5 parts of salt; and boiling water, 5·0 parts. The yellow aq. soln. is fairly stable, but when kept at 100° for a long time, nitrous fumes are slowly evolved. The aq. soln. gives needles of potassium dichlorodinitritoplatinite, $K_2PtCl_2(NO_2)_2$. An excess of chlorine or hydrochloric acid converts the dichlorotetranitritoplatinite into the chloroplatinate. It is decomposed when boiled with a soln. of potassium nitrite, and the normal salt, $K_2Pt(NO_2)_4$, is formed. The salt is soluble in a soln. of potassium chloride, or nitrite. M. Vèzes made **potassium trichlorotrinitritoplatinate,** $K_2Pt(NO_2)_3Cl_3$, by the action of two gram-atoms of chlorine, and a mol of monochlorotrinitritoplatinite; and **potassium pentachloronitritoplatinate,** $K_2Pt(NO_2)Cl_5.H_2O$, by the action of a large excess of hydrochloric acid on a warm conc. soln. of potassium tetranitritoplatinite. M. Vèzes first represented this as a nitroso-salt, $K_2Pt(NO)Cl_5$. C. W. Blomstrand prepared **potassium dibromotetranitritoplatinate,** $K_2Pt(NO_2)_4Br_2$, by the action of bromine on the tetranitritoplatinite; crystals are readily obtained by cooling the hot sat. soln. M. Vèzes, and A. Miolati and I. Bellucci employed a somewhat similar process. The yellow, monoclinic, prismatic crystals were found by H. Dufet to have the axial ratios $a:b:c=1{\cdot}0108:1:1{\cdot}3927$, and $\beta=100°\ 31'$. The salt is not changed in air, or at 100°; it melts and decomposes at dull redness; 100 parts of cold water dissolve 2·5 parts of salt, and boiling water, 50 parts of salt. The yellow soln. is stable, but with prolonged boiling, nitrous fumes are given off. The salt is dissolved. A soln. of potassium nitrite, and crystals of the tetranitritoplatinite are formed; and excess of bromine or hydrobromic acid forms the chloroplatinate. The salt is slightly soluble in a soln. of potassium bromide; and insoluble in alcohol. A boiling soln. in aq. alcohol forms aldehyde, and the dibromodinitritoplatinite. M. Vèzes prepared **potassium tribromotrinitritoplatinate,** $K_2Pt(NO_2)_3Br_3$, from 3 gram-atoms of bromine, as bromine water, and a mol of potassium tetranitritoplatinite in hot, conc. soln. The red prisms were shown by H. Dufet to be rhombic bipyramids with axial ratios $a:b:c=0{\cdot}7344:1:0{\cdot}6524$. The general properties are like those of the corresponding chloro-salt. This salt was first represented as a nitroso-salt, $K_2Pt(NO)(NO_2)_2Br_3$. When the proportion of bromine was increased to 4 gram-atoms, M. Vèzes obtained **potassium tetrabromodinitritoplatinate,** $K_2PtBr_4(NO_2)_2$, in long, red prisms. Their general properties resemble those of the corresponding chloro-salt. M. Vèzes could not make *potassium pentabromonitritoplatinate.* M. Vèzes made **potassium tetraiododinitritoplatinate,** $K_2Pt(NO_2)_2I_4$, by the action of an alcoholic soln. of iodine on the diiododinitritoplatinite at 80°. The conc. soln. on cooling deposits black crystals with a greenish lustre. H. Dufet represented them as rhombic bipyramids with axial ratios $a:b:c=0{\cdot}7874:1:0{\cdot}6430$. M. Vèzes found the crystals are stable in air, and at 100°; they decompose at a dull red-heat; they are sparingly soluble in cold water, but are readily dissolved by hot water; and when the aq. soln. is boiled, the diiododinitritoplatinite is formed. He also made **potassium pentaiodonitritoplatinate,** $K_2Pt(NO_2)I_5$, which he regarded at first as a nitroso-salt, $K_2Pt(NO)I_5$. It was obtained by adding an alcoholic soln. of iodine to a conc. soln. of the diiododinitritoplatinite, and concentrating the soln. at a suitable temp. The black crystals behave very much like those of the preceding salt. A. Miolati and I. Bellucci prepared **silver dibromotetranitritoplatinate,** $Ag_2PtBr_2(NO_2)_4$, by the action of a conc. soln. of silver nitrate on powdered potassium dibromotetranitritoplatinate. The red crystals are sensitive to light.

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§ 39. Nitrogen Peroxide or Tetroxide

The ruddy fumes of this compound always appear as a by-product in the old method of preparing nitric acid by heating a mixture of saltpetre with copperas, or alum. Consonant with the language of the alchemists, W. Clark[1] referred, in 1670, to the red vapours which are formed when saltpetre is heated in a retort as *the flying dragon*. In 1778, P. J. Macquer regarded the red vapours as an essential constituent of nitric acid itself, and asked : *Pourqoi les vapeurs de cet acide sont-elles rouges ?* He was not satisfied with the earlier explanations. About the beginning of the eighteenth century, both C. A. Baldiun, and G. E. Stahl had attributed the red fumes to the presence of a peculiar substance—*anima nitri*—in saltpetre. About twenty years later, J. H. Pott said that the red fumes are of an oily, sulphurous nature because charcoal burns with a flame in the vapours. J. C. Wiegleb attributed the red colour to the presence of elemental fire. In 1736, J. Hellot mistook an accidental impurity for an essential constituent, for he said that the colour is due to the rarefaction of the ferruginous particles in *les vapeurs de l'esprit de nitre* during the distillation. C. W. Scheele inquired whether the vapours of nitric acid are naturally red, and he inferred from his experiments that if nitric acid be associated with a little phlogiston, it furnishes the red vapours ; but if it be associated with more phlogiston, it forms a colourless gas (nitric oxide). This explanation, translated into modern language, was getting nearer the truth, for it means that the red gas is an intermediate stage of oxidation between that of nitric acid and that of nitric oxide. Pure colourless nitric acid was called dephlogisticated nitric acid. J. Priestley, and H. Cavendish showed that the red fumes obtained when nitrous air comes in contact with atmospheric air have an acidic nature ; and J. Priestley called the red gas *nitrous acid air*. A. L. Lavoisier inferred from his experiments : *Sur l'existence de l'air dans l'acide nitreux*, that nitric acid is a compound of nitric oxide and oxygen, while the red fume is a compound of nitric oxide and nitric acid. In 1816, the work of J. L. Gay Lussac, J. J. Berzelius, P. L. Dulong, and E. Péligot established the relations between the red vapours, nitric oxide, nitrous oxide, and nitrous and nitric acids. They called the gas *l'acide hypoazotique;* it is now known as **nitrogen peroxide,** or **nitrogen tetroxide,** N_2O_4, or NO_2.

The preparation of nitrogen peroxide.—The oxidation of nitric oxide to nitrogen peroxide has been previously discussed. Some of the methods indicated in connection with the oxidation of nitrogen furnish nitrogen peroxide. Thus, the Société d'Études Minières et Industrielles[2] prepared nitrogen peroxide by the interaction of ammonia and oxygen, air, or oxygenated air in the presence of rhodium as catalyst. S. Genelin said that half an hour's sparking of air in a eudiometer tube can be arranged so as to show the formation of nitrogen peroxide by the colour of the vapour. J. L. Gay Lussac prepared nitrogen peroxide by mixing nitric oxide with half its vol. of oxygen. P. L. Dulong passed the dry-mixed gases through a tube packed with pieces of porcelain, and then through a U-tube cooled to about 20°. The green liquid becomes yellow even on decantation. E. Péligot said that the gases cannot be properly dried by calcium chloride, and he recommended passing the mixed gases first through conc. sulphuric acid, then through a tube packed with solid, recently fused, potassium hydroxide, and lastly into a receiver cooled to —15° or —20°. Under these conditions, the product forms colourless crystals. After a time, the potassium hydroxide loses its desiccating powers, and if the operation is continued, the crystals deliquesce, forming a green liquid which gradually darkens in colour and becomes more volatile.

According to F. Raschig, the red vapours formed by the action of air on nitric oxide are different from ordinary nitrogen tetroxide and he called the product *nitrogen isotetroxide,* N=O=O, to distinguish it from the ordinary tetroxide. He said that the isoperoxide is the primary product when nitrogen is burnt in the high-tension arc, or when ammonia is burnt with a platinum catalyst at a low red-heat. This is contrary to the idea that nitric oxide is the only nitrogen oxide stable at a high temp. The lighter colour observed when nitrogen peroxide is passed through a hot tube is not to be attributed to its decomposition into nitric oxide and oxygen, but to the formation of the lighter coloured isoperoxide. While the ordinary tetroxide reacts with sodium hydroxide: $N_2O_4+2NaOH=NaNO_2+NaNO_3+H_2O$, he said that the iso-compound reacts: $N_2O_4+2NaOH=2NaNO_2+H_2O+O$. If a large excess of oxygen is used in oxidizing the nitric oxide, he added that a *nitrogen isopentoxide* as well as *nitrogen hexoxide,* N_2O_6, reacts with alkali-lye: $N_2O_5+2NaOH=NaNO_2+NaNO_3+H_2O+O$; $N_2O_6+2NaOH=2NaNO_2+H_2O+3O$; and $N_2O_7+2NaOH=NaNO_2+NaNO_3+H_2O+3O$. These hypothetical compounds were not confirmed by E. Müller.

J. L. Gay Lussac made nitrogen peroxide by heating dry lead nitrate in a retort connected with a cooled receiver. P. L. Dulong said that the liquid so obtained is anhydrous, or contains at most 0·6 per cent. of water. E. Péligot found that a greenish liquid first passes over, then a colourless liquid containing but a small proportion of water, and lastly the anhydrous compound which solidifies in crystals. K. Heumann recommended mixing the lead nitrate with its own vol. of sand previously calcined. When nitrogen trioxide is decomposed, nitrogen peroxide is formed; and the same remark applies to other nitrogen oxides, to nitrous acid, silver nitrite, and many nitrates. L'Azote Français Société Anon. obtained nitrogen peroxide by heating calcium nitrate above 500° and below 650° in the presence of oxygen. M. Berthelot found nitrogen pentoxide decomposes into nitrogen peroxide when exposed to light; and the gas is also formed when nitric acid vapour is passed through a red-hot tube. A. Bogorodsky found that fused alkali nitrates give off nitrogen peroxide when electrolyzed. P. Winand obtained nitrogen peroxide by the addition of fuming sulphuric acid to a fused mixture of alkali nitrite and nitrate: $NaNO_2+NaNO_3+H_2S_2O_7=2NaHSO_4+2NO_2$—sufficient sodium hydrosulphate is added from a previous preparation to fix any free sulphur trioxide, $2NaHSO_4+SO_3=Na_2S_2O_7+H_2SO_4$.

According to E. Mitscherlich, when fuming nitric acid is gently heated in a retort connected with a receiver surrounded by a freezing mixture, two immiscible layers of liquid are obtained. The lower one is a soln. of nitrogen peroxide in some hydrated nitric acid, and the upper one, a soln. of monohydrated nitric acid in nitrogen peroxide. When the latter is redistilled, nitrogen peroxide of a high degree of purity is obtained. J. Fritzsche said that in the preceding preparations, the nitric acid should be removed from the nitrogen peroxide by redistillation. C. W. Hasenbach, A. Guether, and G. Lunge obtained nitrogen peroxide by the action of conc. nitric acid of sp. gr. 1·38, or of red fuming nitric acid of sp. gr. 1·45 to 1·40, on arsenic trioxide, and condensing the product in the usual way—*vide supra,* nitrogen trioxide. According to C. W. Hasenbach, the nitrogen trioxide can be removed from the condensed liquid by passing oxygen through it; or, according to L. Playfair and J. A. Wanklyn, by distillation from potassium chlorochromate. C. W. G. Nylander believed that an isomeric form of the peroxide is obtained by this process; but C. W. Hasenbach denied this. G. Lunge used starch in place of arsenic trioxide—*vide supra,* nitrogen trioxide; and L. Vanino recommended formaldehyde or paraformaldehyde in place of arsenic trioxide. P. C. Freer and G. O. Higley obtained the gas by dissolving many metals—copper, silver, iron, etc.—in nitric acid of a suitable conc.—*vide* the metals. The gas is also formed when straw, sawdust, and various organic substances are treated with fuming nitric acid.

W. Ramsay showed that nitrogen peroxide is formed by mixing nitrogen tri- and penta-oxides. It suffices to pour a soln. of phosphorus pentoxide in well-cooled nitric acid into liquid nitrogen trioxide. The blue colour disappears, and the liquid can be decanted off and distilled. A. C. Girard and J. A. Pabst, and J. P. Park and J. R. Partington obtained nitrogen peroxide by heating nitrosyl sulphonate (chamber crystals) with potassium nitrate: $NO_2.HSO_3+KNO_3=2NO_2+KHSO_4$; by treating nitrous acid or a nitrite with nitric acid: $HNO_3+RNO_2=2NO_2+R.OH$; or by treating nitrosyl chloride with nitric acid: $NOCl+HNO_3=2NO_2+HCl$; A. Exner, by the action of nitroxyl chloride on silver nitrite: $NO_2Cl+AgNO_2=AgCl+2NO_2$; C. Weltzien, by the action of iodine on silver nitrate; and F. Kuhlmann, by passing a mixture of cyanogen and air through a red-hot tube containing platinum sponge. A. Stavenhagen and E. Schuchard observed that some nitrous oxide is transformed into nitrogen peroxide during the combustion of sulphur in that gas (*q.v.*).

The physical properties of nitrogen peroxide.—Nitrogen peroxide forms a yellowish-red vapour which was formerly regarded as a permanent gas because it was not readily condensed by cold. This was due to the fact that the vapour was mixed with air. The **colour** undergoes some extraordinary changes with variations of temp. P. L. Dulong[3] said that the liquid at —20° is colourless; at —10°, almost colourless; between 0° and 10°, pale yellow; and from 15° to 28°, orange-yellow. As the temp. rises, the colour becomes darker and darker. C. F. Schönbein found that at —50°, the crystals are colourless; between —40° and —30°, pale yellow; between —30° and —20°, pale lemon-yellow; and at the m.p., —20°, pale honey-yellow. H. St. C. Deville and L. Troost, and C. F. Schönbein said that the vapour at —10° is faintly yellow, and with rise of temp. the colour deepens; it is reddish-brown, and at 183°, a 2-cm. layer of the gas is opaque and almost black. At higher temp., the colour becomes paler because the gas is then decomposed into oxygen and nitric oxide. The colour changes are all reversed by cooling. L. Playfair and J. A. Wanklyn found the **vapour density** fell from 2·588 at 4·2° to 1·783 at 97·5°. Related observations were made by R. Müller, H. St. C. Deville and L. Troost, E. and L. Natanson, K. Schreber, M. Bodenstein and M. Katayama, J. W. Gibbs, A. J. Swart, W. L. Argo, S. Dushman, L. Troost, A. Naumann, and A. Richardson. It is assumed that the colour changes, and the variation in the vapour density are due to the variation in the state of equilibrium with temp.: $N_2O_4 \rightleftharpoons 2NO_2$. The condition of equilibrium is $K=C^{\frac{1}{2}}/C_1$, where C denotes the conc. of the N_2O_4-mols., and C_1, that of the NO_2-mols. It is found that at 0°, K=8·060; at 18·8°, 3·710; at 49·9°, 1·116; at 73·6°, 0·544; and at 99·8°, 0·273. The compound with the more complex mol. N_2O_4 is colourless, and with the simpler mol. NO_2, black. This phenomenon is difficult to explain by the theories on the relation between colour and chemical constitution. Assuming that the vapour density is dependent on the degree of **dissociation**, H. St. C. Deville and L. Troost calculated the percentage dissociation, α, from the vapour density, D, and also the change in the degree of dissociation, $\delta\alpha/\delta t$, per 10° rise of temp.:

	26·7°	39·8°	60·2°	80·6°	100·1°	121·5°	135·0°
D . .	2·65	2·46	2·08	1·80	1·68	1·62	1·60
α . .	19·96	29·23	52·84	76·61	89·23	96·23	98·69
$\delta\alpha/\delta'$ . .	6·5	11	13	10·4	4·4	3·5	1·8

The vapour density at 183·2° was 1·57. G. Salet compared the colour changes at different temp. on the assumption that the gas with N_2O_4 mols. alone is colourless, and found the calculated proportions agreed with those obtained by the vapour density method. The other physical properties of the gas agree with the assumed polymerization. J. T. Cundall found that polymerization occurs with the soln. of the gas in chloroform, bromoform, methylene chloride, ethylene chloride, ethylidene chloride, ethylene bromide, ethyl bromide, carbon tetrachloride, carbon disulphide, acetic acid, benzene, chlorobenzene, bromobenzine, and silicon tetrachloride. The nitrogen peroxide dissociates when diluted with chloroform just as the gas does when diluted with an indifferent gas, or when the press. is reduced. Similarly, the dissociation increases with rise of temp. Only 1·22 per cent. of the peroxide is dissociated into NO_2-mols. at 25°. At 10°, 20°, and 30°, the dissociation with chloroform is 7·7, 14·5, and 26·2 respectively; and it is nearly the same with the other solvents except that with acetic acid, it is 2·3, 4·6, and 8·5 respectively; with carbon disulphide, 12·2, 22·5, and 38·3 respectively; and with silicon tetrachloride, 15·7, 26·0, and 52·0 respectively. W. Ramsay found the mol. wt. of nitrogen peroxide in acetic acid agrees with the value for the N_2O_4-mol. W. Ostwald represented the amount of dissociated peroxide by s; the undissociated peroxide, by $1-x$; the vol. of unit mass by v; the equilibrium constant by K; and found that for equilibrium, $x^2=v(1-x)K$. Using J. T. Cundall's results for dil. soln.:

v .	3·8	4·4	5·7	6·5	7·0	8·7	11·2
x .	0·00178	0·00206	0·00657	0·00304	0·00328	0·00407	0·00524
K .	$0·0_6312$	$0·0_6254$	$0·0_6257$	$0·0_6231$	$0·0_6215$	$0·0_6228$	$0·0_6220$

The constancy of K within the limits of experimental error, shows that nitrogen peroxide dissociates in accord with the law of mass action whether in dil. soln., or in the gaseous state. A. Colson's results did not agree with the simple equation $N_2O_4 \rightleftharpoons 2NO_2$; A. Langevin attributed this to A. Colson not having worked with sufficiently dil. soln. Complex addition products of nitrogen peroxide are known to exist, and accordingly, P. Paschal was led to try if, at low temp., it can be obtained in a higher state of polymerization than N_2O_4; but he found that even at −68°, there is no evidence that the molecules are more complex than they are in the ordinary liquid state. E. Grüneisen and E. Goens calculated that every N_2O_4-molecule on the average dissociates at least once every ten-thousandth of a second; and H. Selle, that a mol of N_2O_4 at 21° and 500 mm. press. dissociates to the extent of 4·4 per cent. in 10^{-4} second, and a mol of NO_2 associates to N_2O_4 to the extent of 4·6 per cent. in 10^{-8} second. A. K. Brewer noticed ionization occurs during the decomposition of the peroxide at 385°; H. Staudinger and W. Kreis tried unsuccessfully to isolate solid NO_2 by suddenly chilling the gas from 1000° to −190°.

According to A. Richardson, the vap. density of nitrogen peroxide at 140° corresponds exactly with the formula NO_2, and at higher temp., the vap. density becomes smaller until 5 per cent. of the peroxide is dissociated at 184°; 13 per cent. at 279°; 56·5 per cent. at 494°; and at 619·5°, it corresponds with the completion of the change $2NO_2 \rightarrow 2NO+O_2$. Hence, as soon as the change $N_2O_4 \rightarrow 2NO_2$, is nearing completion, the decomposition of the product begins. W. Ramsay and J. T. Cundall also showed that the bleaching of the black NO_2-gas at elevated temp. is due to its dissociation $2NO_2 \rightleftharpoons 2NO+O_2$. M. Bodenstein and M. Katayama represented the equilibrium conditions of this reaction by $[NO_2]^2K=[NO]^2[O_2]$, and found for the percentage dissociation at different temp.:

	222°	279°	390°	448°	485°	494°	619°
Dissociation . .	4·17	13·10	35·05	40·63	57·48	58·71	100
log *K* . . .	−6·029	−4·523	−3·110	−2·776	−2·167	−2·159	—

The equilibrium constant for partial press. is $\log K = -27400/4{\cdot}571T + 1{\cdot}75 \log T + 3$; or for conc., $\log K_2 = -27400/4{\cdot}571T + 1{\cdot}75T + 4{\cdot}086$. I. W. Cederberg used the equations $\log K_p = -6126T + 2{\cdot}5 \log T + 1{\cdot}316$; and $\log K_c = -6126 \mid T + 1{\cdot}5 \log T + 2{\cdot}402$. E. Wourtzel found that the dissociation constant between 0° and 86·5° can be represented by $\log K = 8{\cdot}9908T - 2810{\cdot}5$.

E. and L. Natanson measured the effect of temp., θ, and press., p mm., on the vap. density, D, of the gas. The following is a selection from their results:

	0°				21°			
p .	37·96	86·57	172·48	250·66	491·60	516·96	556·50	639·70
D .	248·32	2·6737	2·8201	2·9028	2·6838	2·7025	2·7120	2·7459

	49·7°				73·7°			
p .	26·80	93·75	182·69	261·37	49·65	107·47	302·04	633·27
D .	1·6634	1·7883	1·8942	1·9629	1·6315	1·6601	1·7403	1·8534

	99·8°				129·9°			
p .	11·73	79·57	202·24	732·51	35·99	78·73	247·86	550·29
D .	1·6029	1·6179	1·6263	1·6923	1·5987	1·5986	1·6012	1·6084

at 151·40°, the value of p and D were respectively 117·98, 1·5907; 475·41, 1·5882; and 666·22, 1·5927. The **vapour pressure** of nitrogen peroxide has been measured by P. A. Guye and G. Drouginine, F. Russ and E. Eberwein, etc. A. C. G. Egerton found for the vap. press., p mm., of the solid, between −30° and −100°:

	−30°	−40°	−50°	−60°	−70°	−80°	−90°	−100°
p . .	39·24	9·77	2·44	0·605	0·151	0·036	0·0093	0·0023

which he represented by $\log p = 14{\cdot}9166 + 0{\cdot}0604\theta$; or $\log p = -2069T^{-1} + 1{\cdot}75 \log T - 0076T + 4{\cdot}6$; and for the liquid, he gave $\log p = -2211T^{-1} + 1{\cdot}75 \log T - 0{\cdot}0049T + 4{\cdot}6$; and $\log (147/p) = 4{\cdot}2\{(171{\cdot}2/T) - 1\}$. F. Russ and E. Eberwein gave for the vap. press. of the liquid $\log p = -2625{\cdot}2T^{-1} + 1{\cdot}75 \log T - 0{\cdot}007T$ between −80° and −10·8°. F. E. C. Scheffer and J. P. Treub observed the vap. press., p mm., of the liquid to be:

	−36°	−23°	−23°	−10°	−0·6°	7·7°	15°	27·4°	43·2°
p .	18	53	70	146	180	293	565	1007	1982
	Solid.		Liquid.						

A. Mittasch and co-workers found the vap. press. of the liquid to be:

	3·2°	10·3°	19·9°	29·95°	39·85°	48·95°
p . .	319·5	455·5	721	1133·5	1737	2522 mm.

After an intensive drying of nitrogen tetroxide for 25 months, A. Smits and co-workers found that the vap. press. rose to 19 mm. A part of the liquid was distilled off and the increase in vap. press. then fell to 4 mm., but after a further 11 days this had risen to 14·7 mm., *i.e.* it had nearly regained its value before distillation. The colour of the intensively dried liquid was a deeper brownish-red than of the "moist" liquid. The changes of both the vap. press. and the colour agree with the assumption that the drying process had effected a displacement of the internal equilibrium in the direction $N_2O_4 \rightarrow 2NO_2$. J. W. Smith also observed an increase in the vap. press. of nitrogen tetroxide during intensive drying; this amounted to about 25 mm. The change is slow. If the temp. be suddenly changed it requires some hours for equilibrium to be attained. P. L. Dulong gave 1·451 for the **specific gravity** of liquid nitrogen peroxide; A. Geuther found 1·5035 at −5°; 1·4935 at

0° ; 1·4880 at 5° ; 1·4770 at 10° ; and 1·4740 at 15° ; O. Scheuer, 1·4905 at 0° ; T. E. Thorpe, 1·4903 at 0°, and 1·43958 at 21·6° ; and W. Ramsay and J. Shields, 1·4856 at 1·6°, and 1·444 at 19·8°. A. Mittasch and co-workers gave for the sp. gr., *D*, of the liquid :

	(0°)	10·3°	21·05°	29·95°	39·9°	48·95°	54·4°	(60°)
Sp. gr. .	1·4906	1·4688	1·4433	1·4227	1·3976	1·3745	1·3562	1·3435

P. Pascal and M. Garnier represented the sp. gr., *D*, of liquid nitrogen peroxide at $\theta°$, between 0° and 21·5°, by $D=1·490-0·00215\theta$. W. R. Bousfield represented the specific volume of the liquid, at $\theta°$, between 0° and 20° by the equation Sp. vol.$=0·67027+0·0010075\theta+0·0_33\theta^2$. E. Rabinowitsch gave 63 for the mol. vol. T. E. Thorpe and J. W. Rodger represented the **viscosity,** η, at $\theta°$, by $\eta=28·155(140·89+\theta)^{-1·7349}$, when the observed values were 0·005220 at 0·72° ; 0·004720 at 9·15° ; and 0·00401 at 15·36°. W. Ramsay and J. Shields found the **surface tension** to be 29·52 dynes per cm. at 1·6°, and 26·56 at 19·8°. Hence the mol. **surface energy** $\sigma(Mv)^{\frac{2}{3}}$ is 29·52 ergs at 1·6°, and 26·56 ergs at 19·8°. Hence, the liquid is not further polymerized than N_2O_4. A. C. G. Egerton gave 4·6 for the **chemical constant.** Measurements of the **velocity of sound** in the gas were made by W. L. Argo, E. and L. Natanson, and F. Keutel. H. Selle obtained 186·41 metres per second, and E. Grüneisen and E. Goens, 184·3 metres per second. E. Grüneisen and E. Goens measured the velocity of sound in the gas at various temp. and press., and found that with frequencies of the order 15,000 per second, there is no indication that the velocity of sound depends on the frequency, as should be the case if the time required for setting up the dissociation equilibrium were comparable with the vibration period of sound. The absolute value of the velocity of sound agrees much better with the assumption that the time required for the setting up of a dissociation equilibrium is small in comparison with the vibration period. Measurements at 25° and 760 mm. show that the velocity constant of the decomposition, *k*, under the experimental conditions is larger than 10,000 ; consequently, every mol. of nitrogen peroxide dissociates on the average at least once in every 10^{-4} sec. E. Drion, and T. E. Thorpe measured the **thermal expansion** of the liquid. The latter found by interpretation, starting with unit vol. at 0° :

	0°	5°	10°	15°	20°	21·64°
Vol. . .	1·00000	1·00789	1·01573	1·02370	1·03196	1·02523

and he represented the vol., *v*, at $\theta°$, by $v=1+0·0015910\theta-0·0_5397015\theta^2+0·0_62153\theta^3$. C. Feliciani found 0·0033 for the coeff. of **thermal conductivity** at 150°, and said that at all press. the conductivity rises from 18° to a maximum at 65° ; this is followed by a decrease to a minimum, with a second maximum between 120° and 130°. The conductivity increases with press., and the conductivity and dissociation follow the similar courses ; for press. not less than 60 mm., the conductivity of nitrogen peroxide up to 90° is larger than that of any non-dissociating gas previously examined. The results by G. Magnanini and G. Malagnini, and W. Nernst are considered to be unsatisfactory.

M. Berthelot and J. Ogier gave for the **specific heat** of nitrogen peroxide $c_p=1·625$ between 27° and 67° ; 1·115 between 27° and 150° ; and 0·65 between 27° and 280°. K. Schreber calculated from M. Berthelot and J. Ogier's results that the molecular heats of N_2O_4-gas are $C_p=14·85$ Cals. ; $C_v=12·85$; and the ratio of the two sp. hts., 1·555 ; while for NO_2-gas, $C_p=8·43$; $C_v=6·43$; and for the ratio of the two sp. hts., 1·31. According to E. D. McCollum, the mol. ht. of N_2O_4 is slightly greater than that of NO_2. E. and L. Natanson obtained 1·172 for the ratio of the two sp. hts., at about 20°, of the gas when 15·07 per cent. was dissociated, and 1·274 when 56·99 per cent. was dissociated. They also found for NO_2, 1·31. The value 1·172 is near that usually obtained for gases with pentatomic or polyatomic molecules, while 1·274 comes near that usually obtained for gases with triatomic molecules. Measurements of the ratio of the two sp. hts. were made by J. A. Swart, F. Keutel, W. L. Argo, H. Selle, and E. Grüneisen and E. Goens, making allowance for the degree of dissociation of the gas. W. Ramsay found that liquid nitrogen peroxide has a sp. ht. 0·477 ; and the solid, 1·0. G. Piccardi studied the thermal capacity of nitrogen peroxide.

E. Péligot gave 22° for the **boiling point** ; J. L. Gay Lussac, 26° ; P. L. Dulong, 28° at 760 mm. ; and C. W. Hasenbach prepared 22° for the gas obtained from lead nitrate, and this value was raised to between 25° and 26° after the passage of oxygen through the liquid. G. Lunge and E. Berl, 20° at 720 mm. ; G. Oddo, 22°–23° ; A. Nadejdine, 22·5° at 750·4 mm. ; A. Geuther, and G. Bruni and P. Berti, 26°. T. E. Thorpe gave 21·64° at 760 mm. ; T. E. Thorpe and J. W. Rodger, 21·97° ; and F. E. C. Scheffer and J. P. Treub, 21·2° ; P. A. Guye and G. Drouginine, 22° ; and W. R. Bousfield, 21·9°±0·1°. These numbers are not very concordant. H. B. and M. Baker found that when the liquid is thoroughly dried it suffers no apparent change at the b.p., and liquid is still visible at 69° and 757 mm., when no boiling occurred, though evaporation occured. A. Smits attributed the phenomenon to the presence of active and inactive molecules : $\alpha\text{-}N_2O_4 \rightleftharpoons \beta\text{-}N_2O_4$, and assumed that intense drying resulted in the shifting of the equilibrium to the inactive side. E. Péligot said that the liquid freezes to colourless prisms at —20° ; and he gave —9° for the **melting point** ; J. Fritzsche gave —13·5° ; R. Müller, —11·5° to —12° ; W. Ramsay, —10·14° ; G. Bruni and P. Berti, —10·95° ; H. St. C. Deville and L. Troost, —10° ; F. E. C. Scheffer and J. P. Treub, —10·8° ; G. Oddo, —9·04° ; A. C. G. Egerton, —10·5° ; and P. A. Guye and G. Drouginine, —9·6°. E. Péligot said that after being melted, the peroxide requires a much lower temp. for its solidification, for at —16° the compound remains liquid, and J. Fritzsche said that it can be re-solidified only at —30° because a little nitric acid has been formed, and this also accounts for the turbidity of the cooling liquid. For the fusion curve with nitric oxide, *vide supra*, nitrogen trioxide. P. Pascal studied the f.p. of binary systems of nitrogen peroxide with bromoform, chloroform, carbon tetrachloride, bromobenzene, methyl iodide, chloropicrin, and camphor. F. E. C. Scheffer and J. P. Treub gave 158·2° for the **critical temperature,** and 100 atm. for the **critical pressure** ; and it was estimated that at the critical temp. the molecules are all NO_2. W. Ramsay calculated that the latent **heat of fusion** is between —32·2 Cals. and —37·2 Cals. A. C. G. Egerton calculated 9·586 Cals. between —23° and —26°. The latent **heat of vaporization** is 4·3 Cals. at 180° ; F. E. C. Scheffer and J. P. Treub gave 9·2 Cals. at the b.p. ; and A. C. G. Egerton, 9·458 Cals. N. de Kolossowsky gave 1·37 to 2·58 for the **ebulliscopic constant.**

M. Berthelot gave for the **heat of formation,** $(N,O_2)=-7{\cdot}6$ Cals. in the gaseous state ; and 3·4 Cals. in the liquid state. J. Thomsen gave $(2N,4O)=-3{\cdot}9$ Cals. ; $(NO,O)=19{\cdot}568$ Cals. M. Bodenstein and M. Katayama gave $(2NO,O_2)=-27{\cdot}4$ Cals. ; M. Berthelot, 28 Cals. W. Vaubel calculated the **heat of dissociation** of N_2O_4 to be 104·9 Cals. ; M. Berthelot and J. Ogier, 106 Cals. ; and K. Schreber obtained —12·9 Cals. or at T° K, $Q=13132+2T$ cals. ; and J. Thomsen, —13 Cals. M. Berthelot calculated for undissociated N_2O_4, —2·65 Cals. ; and for NO_2, —8·125 Cals. The heat of formation of the liquid is —2·2 to —2·5 Cals. E. Wourtzel gave 12·85 Cals. for the heat of polymerization. J. C. Thomlinson calculated what he called the thermochemical eq. and used the results in comparing the valency of the nitrogen atom in the different nitrogen oxides.

The **index of refraction** of the vapour of nitrogen peroxide at 36° was found by P. L. Dulong to be 1·000503 ; and by C. and M. Cuthbertson, who estimated from their results that the NO_2-gas has the index of refraction $\mu=1{\cdot}000509$, and the N_2O_4-gas $\mu=1{\cdot}001123$, showing that polymerization increases the refractivity $(1-\mu)$ by about 10·5 per cent. The dispersion power of the NO_2-gas in the red and green is much greater than for the N_2O_4-gas. J. H. Gladstone found the **atomic refraction,** 11·8 ; and the **atomic dispersion,** 0·82. W. H. Bair, and H. O. Kneser studied the **spectrum** of the peroxide. The **absorption spectrum** of nitrogen peroxide was examined by A. J. Weiss, E. Luck, J. Zenneck and B. Strasser, F. Daniels, B. Hassenberg, D. Gernez, J. Chappius, and G. D. Liveing and J. Dewar. According to C. F. Schönbein, the higher the temp. of the gas, the greater the number of lines in the absorption spectrum ; and L. Bell said that the gas at 0° gives no absorption spectrum and inferred that the observed absorption spectrum of nitrogen peroxide is produced by the NO_2-mols. and not by the N_2O_4-mols. A. Kundt found that liquid nitrogen peroxide shows five absorption bands between the green and the red ; and these coincide with the strong marked lines in the spectrum of the gas. If the liquid is cooled, two more bands appear in the green ; and if warmed, bands appear in the red as the liquid becomes brown. Beyond the green there is complete absorption. W. N. Hartley, and S. W. Leifson studied the ultra-violet spectrum ; and F. Daniels, the ultra-red spectrum between 2μ and 7μ, and found that the maxima of the absorption bands are not shifted by the process of dissolution in organic liquids—*e.g.* chloroform, and dichloroethane—the slight shifts of $0{\cdot}05\mu$ observed are due to concentration effects. The results are supposed not to support the radiation hypothesis of chemical action.

J. J. Bogusky found that the **electrical conductivity** of nitrogen peroxide gas is poor, and it is an insulator above 70°. L. Bleekrode also found that the liquid is a poor conductor. In 1840, M. Faraday found the liquid obtained by distilling dry lead nitrate was a poor conductor, but readily conducted when water was present. J. J. Bogusky showed that if the liquid is warmed from 0° to 1°, there is an abrupt change in the resistance which is supposed to be due to the dissociation of the N_2O_4-mols. R. Heberlein observed a continuous change in the conductivity with temp. :

	−10°	0°	10°	20°	30
Resistance .	8·6	12·8	10·2	7·0	$5{\cdot}7 \times 10^6$ ohms
Conductivity	1·16	7·83	9·75	14·2	$17{\cdot}6 \times 10^{-8}$ mho

M. Tenani found that the presence of nitrogen peroxide facilitates the discharge of an insulated positively charged disc, but impedes that of a negatively charged disc. This is attributed to the absorption of light by the nitrogen peroxide which prevents it reaching the metallic disc, the conduction being affected only by the ions formed by the action of the absorbed light in the body of the gas. G. Gehlhoff studied the cathode fall of potential of the gas in a vacuum tube. K. Bädeker found that for the press. ranging from 741 to 747 mm., the **dielectric constants** of the system $N_2O_4 \rightleftharpoons 2NO_2$ with 31, 55, and 85 per cent. dissociation are 1·00229, 1·00144, and 1·00128 respectively at 42·5°, 63·1°, and 92·1°. T. Soné gave $4{\cdot}5 \times 10^{-6}$ for the sp. **magnetic susceptibility** of nitrogen peroxide, NO_2, and $-0{\cdot}28 \times 10^{-6}$ for liquid N_2O_4.

The chemical properties of nitrogen peroxide.—The gas has a sweetish yet sharp odour ; and it tastes and reacts acidic. It colours the skin yellow. The vapour is very injurious, it produces inflammation of the respiratory organs, and death. The physiological action was discussed by C. Duisburg.[4] J. Priestley, J. Raon de Luna, and O. Rebuffat used it as a disinfectant ; and B. Moore and J. T. Wilson, for bleaching flour ; and for explosions, *vide infra*, the action of carbon disulphide. W. Ramsay, and G. Bruni and P. Berti found that liquid nitrogen peroxide acts as **an associating solvent.** P. F. Frankland and R. C. Farmer studied the electrical conductivity of soln. of various compounds in liquid nitrogen peroxide. They found that it is not an ionizing solvent, and b.p. determinations showed that many substances are associated to double molecules in this solvent. C. D. Niven discussed the electronic structure.

M. Berthelot [5] said that nitrogen peroxide is stable as such towards 500°, but this does not agree with the observation of A. Richardson, C. W. Hasenbach, and W. Ramsay and J. T. Cundall—*vide supra.* R. G. W. Norrish found that there is a slow increase in the press. of nitrogen peroxide illuminated by means of a mercury vapour lamp. The press. becomes normal in the dark ; the change is rapid at first, and afterwards slow. The suppression of the effect by the addition of excess of nitric oxide or oxygen, coupled with the fact that nitric oxide is the more effective agent, points to the establishment of a photochemical equilibrium, $2NO_2 \rightleftharpoons 2NO + O_2$.

Since no atomic oxygen could be detected in the reaction mixture, the reaction appears to be bimolecular, probably by collision between photoactive and an inactive molecules of nitrogen peroxide. A heating effect, due to the recombination of nitric oxide and oxygen and to the absorbed radiation, is also involved. M. Berthelot also found that the electric sparking of the gas results in its decomposition into nitrogen and oxygen. J. Zenneck and B. Strasser found that when a current of the gas is drawn through a long narrow discharge tube while an electrical current from an induction coil is passing, the colour of the glow of nitrogen peroxide varies in different parts of the tube; the succession of colours is orange-yellow, bluish-violet, greenish-yellow, and bright red. J. Zenneck and B. Strasser found that the orange-yellow, greenish-yellow, and bright red glows of the first, third, and fourth stages exhibit spectra which have been recognized as due to nitrogen peroxide, nitric oxide, and nitrogen respectively. In the fourth stage, some oxygen lines are also present. The violet-blue glow of the second stage is probably due to an intermediate labile oxide, its spectrum differing from that of the peroxide by a difference in the relative portion, and from that of nitric oxide by a difference in the relative intensities of the lines. M. Faraday also observed that during the electrolysis of nitrogen peroxide, it is slowly decomposed.

F. Kuhlmann found that when the gas is mixed with an excess of **hydrogen,** and passed over red-hot platinum sponge, it furnishes water and ammonia (*q.v.*). C. W. Hasenbach said that nitrogen peroxide does not unite with **oxygen** either at a high or at a low temp. D. Helbig, and F. Förster and M. Koch said that it is oxidized to nitrogen pentoxide (*q.v.*) by **ozone.** C. F. Schönbein found that with **hydrogen dioxide,** nitric acid is formed. Nitrogen peroxide is decomposed by **water.** R. Weber showed that the gas is completely absorbed by water without the evolution of any nitric oxide; and the soln. contains both nitrous and nitric acids. Nitrogen peroxide has thus the character of a mixed oxide. The reaction with liquid nitrogen peroxide was studied by J. L. Gay Lussac, P. L. Dulong, E. Péligot, and C. F. Schönbein. According to P. L. Dulong, when a small proportion of water is added to the liquid, the blue liquid becomes dark green, but no gas in disengaged; the green colour is due to the formation of nitric oxide which dissolves in the nitrous and nitric acids simultaneously. J. L. Gay Lussac found that as water is gradually added to the blue liquid, the colour changes to green and then to orange-yellow; nitric oxide is copiously evolved during the early additions of water, but none, later on. The first action of water is assumed to result in the formation of nitrous and nitric acids: $2NO_2+H_2O=HNO_2+HNO_3$; the nitrous acid then decomposes: $3HNO_2=H_2O+2NO+HNO_3$. The resultant of these two reactions is then represented: $3NO_2+H_2O=2HNO_3+NO$. A. Sanfourche said that nitrogen peroxide originally forms with water or dil. nitric acid equimolecular quantities of nitrous and nitric acids; the subsequent decomposition of the nitrous acid thus formed is complete only when the concentration of the nitric acid does not exceed 20 per cent.; beyond this, the oxidizing action of the nitric acid on the nitric oxide formed in the decomposition was observed, whilst with 70 per cent. nitric acid simple soln. of the peroxide takes place. C. L. Burdick and E. S. Freed measured the partial equilibrium constant $K=[NO][HNO_3]^2/[NO_2]^3[H_2O]$, for the reaction $3NO_2+H_2O=2HNO_3+NO$, when the concentrations are expressed as partial press. They found, for log K, at 25°, 50°, and 75°, for nitric acid containing p per cent. HNO_3:

HNO_3		24·1	33·8	40·2	45·1	49·4 per cent.
log K	25°	−2·40	−2·39	−2·21	−2·30	−2·38
	50°	−2·55	−2·47	−2·28	−2·34	−2·26
	75°	−2·49	−2·47	−2·35	−2·32	−2·34

The percentage conversion of nitrogen peroxide into nitric acid for different concentrations of nitric acid—per cent. HNO_3 by wt.—with gas containing different proportions of nitrogen peroxide is given in Table XXX. Nitric acid above 50 per cent. HNO_3 is a very poor medium for absorbing and converting the oxides produced when ammonia or nitrogen is oxidized by the usual nitrogen fixation processes. The decomposition of the nitrous acid is favoured by heat; and the evolution of nitric oxide, by the addition of substances which promote the formation of gas bubbles—thus, C. F. Schönbein found that after the evolution of nitric oxide from a mixture of liquid nitrogen peroxide with 5 times its vol. of water has ceased, the evolution of nitric oxide is very violent; if heat be applied, the introduction of pumice-stone, charcoal, or platinum wire is attended by a further evolution of gas. The metals silver, copper, brass, and iron act more rapidly than platinum although these metals are very slightly attacked during the operation. According to J. Fritzsche, if one part of water be added in a fine stream to ten parts of liquid nitrogen peroxide at —20° very little nitric oxide is evolved, and two strata of liquid are formed; the upper one is dark green, the lower one lighter green. The upper liquid begins to boil at 20°, but the b.p. quickly rises to 120°, and a blue liquid collects in the receiver. The lower liquid begins to boil at 17°, but the b.p. rises to 28°, and a greenish-blue liquid collects in the receiver. If the liquid nitrogen peroxide be mixed with more water, very little nitric oxide is evolved, and the lower layer becomes a very dark bluish-green colour; it is then transparent only in very thin layers. R. Heberlein found the electrical resistance, *R* ohms, of mixtures of nitrogen peroxide and water shows a minimum value:

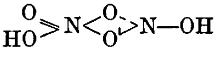
TABLE XXX.—PERCENTAGE CONVERSION OF NITROGEN PEROXIDE TO NITRIC ACID BY ABSORPTION IN AQUEOUS SOLN. OF NITRIC ACID AT ATMOSPHERIC PRESSURE.

HNO_3 Per cent. by wt.	Temp.	Per cent. of nitrogen peroxide in gas.								
		0·1	0·6	1·0	2·0	4·0	6·0	8·0	10	20
5	10	59·8	64·5	65·1	65·7	66·1	66·2	66·3	66·3	66·4
	25	57·1	63·3	64·4	65·3	65·7	65·9	66·1	66·2	66·3
	50	48·8	60·0	61·8	63·7	64·8	65·2	65·4	65·6	66·0
	75	32·6	53·0	56·8	60·2	62·7	63·6	64·2	64·6	65·3
15	10	48·0	60·3	61·6	64·0	64·8	65·2	65·4	65·6	66·0
	25	35·6	55·8	58·7	61·7	63·5	64·1	64·7	65·0	65·5
	50	14·9	43·9	49·8	56·2	59·4	61·2	62·3	63·0	64·3
	75	2·4	24·2	32·6	44·0	51·5	55·0	57·1	58·4	61·5
25	10	31·3	53·7	57·0	60·5	62·7	63·8	64·1	64·5	65·3
	25	17·7	44·2	50·0	56·4	59·6	61·2	62·1	62·9	64·2
	50	2·2	23·7	32·4	44·8	51·2	54·6	56·4	57·7	61·3
	75	0·2	5·9	11·8	23·6	35·0	41·8	45·2	48·2	54·8
35	10	14·6	41·8	47·6	53·8	57·8	59·8	61·0	61·8	63·4
	25	3·0	26·8	34·0	44·4	51·0	54·4	56·4	58·0	61·0
	50	0·3	6·3	12·3	25·6	35·8	41·8	45·2	48·2	54·8
	75	—	0·8	2·2	18·0	16·5	23·4	28·0	32·4	43·6
45	10	2·2	20·4	28·2	38·0	45·8	49·7	52·0	53·5	57·6
	25	0·4	7·4	12·0	22·5	33·3	38·4	42·1	44·6	52·0
	50	—	0·8	2·1	7·2	16·6	21·6	26·0	29·6	41·2
	75	—	—	0·3	1·1	4·0	7·1	10·5	13·6	25·7
55	10	—	2·7	5·2	11·5	17·9	22·0	26·2	27·7	32·6
	25	—	0·7	1·5	4·1	19·3	13·3	16·7	19·5	28·1
	50	—	—	0·2	0·9	2·8	5·0	8·4	9·4	18·9
	75	—	—	—	—	0·5	1·1	2·0	2·6	8·0
65	10	—	—	0·2	0·4	0·8	1·2	1·6	1·9	3·2
	25	—	—	—	—	0·5	0·8	1·1	1·5	3·0
	50	—	—	—	—	—	—	0·6	0·8	1·5
	75	—	—	—	—	—	—	—	—	—

N_2O_4	3·1	10·7	25·4	31·1	49·0	64·0	98·0 per cent.
R 0°	12·0	4·56	2·85	2·76	3·25	3·80	10·40
R 20°	8·40	3·33	2·14	1·99	2·30	2·69	8·0

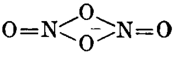
E. T. Chapman supposed that nitrogen peroxide reacts with water, forming nitric acid and nitric oxide: $3N_2O_4+2H_2O=4HNO_3+2NO$; A. V. Harcourt emphasized the fact that some nitrous acid is always formed: $N_2O_4+H_2O=HNO_3+HNO_2$, and that afterwards the nitrous acid is slowly oxidized to nitric acid. The rate of oxidation depends on the temp. and conc. of the acid liquor. L. Troost and P. Hautefeuille said that the heat of oxidation of nitrogen peroxide to nitric acid is 23·5 Cals. per eq. The converse change, the reduction of nitric acid to nitrogen peroxide depends on the conc. of the acid, being 17·5 Cals. per eq. for an acid of maximum sp. gr., 17·1 Cals. for an acid of sp. gr. 1·48, 16·9 Cals. for an acid of sp. gr. 1·46; and 15·3 Cals. for an acid of sp. gr. 1·43. F. Förster and M. Koch showed that the reactions between water and nitrogen peroxide gas are reversible: $2NO_2+H_2O\rightleftharpoons HNO_3+HNO_2$, and $3HNO_2\rightleftharpoons HNO_3+2NO+H_2O$; or summated into one equation, $3NO_2+H_2O\rightleftharpoons 2HNO_3+NO$. Consequently, the partial press. of the nitrogen peroxide, and the nitric oxide correspond with a given conc. of nitric acid. These partial press. are, however, influenced by the equilibrium $NO+NO_2\rightleftharpoons N_2O_3$, and the solubility of the nitrogen trioxide in conc. nitric acid at low temp. In the presence of oxygen, also, there is the disturbance due to the reaction $2NO+O_2=2NO_2$, so that with a given quantity of nitrogen peroxide, the ultimate product is nitric acid. The conc. of the nitric acid formed by the action of a mixture of nitrogen peroxide and oxygen or air on water reaches a limit $2NO_2+H_2O\rightleftharpoons NO_3+HNO_2$, which is a function of the conc. of the nitrogen peroxide, since the lower the partial press. of the peroxide, the smaller the conc. of its soln. in water, and also of its reaction with water. The larger vol. of undissolved gases passing through the soln. causes a more rapid evaporation of water and nitric acid. When soln. containing over 68 per cent. nitric acid are evaporated, the acid volatilizes more rapidly than the water. Consequently, the maximum conc. of nitric acid which can be obtained by the action of a mixture of nitrogen peroxide and oxygen or air on water must be somewhere about this percentage. The limiting conc. of acid must be smaller the more rapid the current of gas. With air containing 1, 2, and 5 per cent. of nitrogen peroxide, the limiting conc. of the resulting nitric acid is about 46, 52, and 55 per cent. respectively. Therefore, the gases obtained by the combustion of nitrogen in the electric arc, containing about 1 or 2 per cent. of nitrogen peroxide, could give 46–52 per cent. nitric acid when absorbed by water. If ozone be present, some nitrogen peroxide is oxidized to pentoxide, and a greater conc. would be attained. E. Briner and E. L. Durand consider that the equilibrium between nitrogen trioxide and peroxide and nitrous and nitric acids involves a trio of reversible processes: $H_2O+N_2O_3=2HNO_2$; $2NO_2+H_2O\rightleftharpoons HNO_3+HNO_2$; and $3HNO_2=HNO_3+2NO+H_2O$. Nitric oxide also reduces nitric acid, and this the more the greater the partial press. of the nitric oxide, and the greater the conc. of the nitric acid. The heats of the reactions are endothermic so that a rise of temp. increases the ratio $HNO_3:HNO_2$. Consequently, a high press. and low temp. favour the formation of nitrous acid, and conversely for nitrous acid. The equilibrium conditions for the reaction $3HNO_2\rightleftharpoons HNO_3+2NO+H_2O$, have been studied by A. V. Schaposhnikoff, and G. N. Lewis and A. Edgar—*vide supra.* O. R. Wulf and co-workers found that the oxidation of nitrogen peroxide by **ozone** at 25° is instantaneous, and the reaction is: $N_2O_4+O_3=N_2O_5+O_2$. A. Pinkus and M. de Schulthess found that the reaction between ozone and nitrogen peroxide takes place with the evolution of light, and very often partakes of the character of an explosion, even when the quantity of ozone present is very small. A very strong bi-polar ionization accompanies the reaction, which appears to be due entirely to the reaction itself, but this is not quite certain, because the product of the reaction, nitrogen pentoxide, is solid, and because of the violence with which the reactions take place.

J. L. Gay Lussac, P. L. Dulong, and F. Raschig showed that aq. soln. of the **alkali hydroxides** react with nitrogen peroxide very much like water. With conc. alkali-lye, a mixture of alkali nitrite and nitrate is formed accompanied by a slight evolution of nitric oxide. The primary reaction is: $2NO_2+2KOH=KNO_3+KNO_2+H_2O$. G. Lunge, and E. Berl found that equimolar proportions of nitrite and nitrate are obtained with dil. soda-lye only when the nitrogen peroxide is in the liquid state, or is diluted with an inert gas. If mixed with air or oxygen, the nitrite is partially oxidized to nitrate. According to M. le Blanc, a mixture of nitric oxide and nitrogen peroxide in equimolar proportions behaves like nitrogen trioxide, which forms with alkali-lye almost pure nitrite: $N_2O_3+2KOH=2KNO_2+H_2O$, while a little nitrate and nitric oxide are formed at the same time. Again, if nitric oxide mixed with air or oxygen be undergoing oxidation, alkali nitrite may predominate, and the shorter the interval of time between the mixing of the gases and the absorption of alkali-lye, the greater the proportion of alkali nitrite formed. The following reactions are supposed to be concerned in the absorption of alkali-lye of a mixture of air and nitric oxide when the latter gas is undergoing oxidation to nitrogen peroxide: (i) $2NO+O_2\rightleftharpoons 2NO_2$; (ii) $NO+NO_2=N_2O_3$; (iii) $2NO_2+2KOH=KNO_3+KNO_2+H_2O$; and (iv) $N_2O_3+2KOH=2KNO_2+H_2O$. The second and last of these reactions take place rapidly. The conc. of nitrogen trioxide is always very small, but, directly the equilibrium is distributed by the absorption of nitrogen trioxide, more trioxide is formed, and this continues until one of the components is exhausted. The third reaction is comparatively slow. F. Förster and A. Blich confirmed these assumptions, and showed that nitrogen trioxide is absorbed by alkali-lye more rapidly than nitrogen peroxide; and consequently, alkali-lye absorbs a mixture of nitric oxide and nitrogen peroxide more rapidly than the latter alone. A. Sanfourche observed that the action of oxides of nitrogen on soln. of alkali hydroxide in which the calculated proportions of nitrate and nitrite are formed only occurs if the alkali is in excess at all points in the soln. Otherwise, a reaction with the water takes place with formation of nitric acid and nitric oxide, the latter being further oxidized if oxygen is present. Moreover, if all the oxides of nitrogen are not absorbed in their first passage through the soln., this reaction with water continues in the gaseous phase with water vap. This is shown by the formation of a nitric acid mist and by its subsequent deposition as acid dew on the upper portion of the walls of the vessel in spite of the presence of excess of alkaline soln. R. Weber showed that salts with **water of crystallization**—*e.g.* alum—slowly decolorize nitrogen peroxide. G. Oddo found that with soln. of water in nitrobenzene, the water forms simple mols. at low conc., and more complex mols. at higher conc.; but with soln. of nitrogen peroxide in nitrobenzene, water gives values for the mol. wt. which at small conc. approaches and subsequently exceeds three times the theoretical number. It is therefore inferred that the gas tends to form **hydrated nitrogen peroxide,** $N_2O_4.H_2O$, which he called **nitrosic acid,** $H_2N_2O_5$. He represented this acid by the formula $O:N(OH):O_2.N(OH)$, and considered its constitution to be related to that of nitrogen peroxide:



$\begin{smallmatrix}O\\HO\end{smallmatrix}\!>N<\begin{smallmatrix}O\\O\end{smallmatrix}\!>N{-}OH$

Nitrosic acid, $H_2N_2O_5$.



$O{=}N<\begin{smallmatrix}O\\O\end{smallmatrix}\!>N{=}O$

Nitrogen peroxide, N_2O_4.

Nitrosic acid can be regarded as a combination of a mol each of nitric and nitrous acids: $HNO_2+HNO_3=H_2N_2O_5$. This is supported by V. H. Veley's observation that lead is attacked to a greater degree by mixtures of nitric and nitrous acids than by either alone, and the reaction with the mixture of acid is the more intense the more nearly equal is the proportion of nitric and nitrous acids. G. Oddo said that the basic function of the :N.OH-group tends to convert nitrosic acid by way of the ammonium salt into the anhydride; nitrogen peroxide can thus be regarded as nitrosic anhydride. Although this acid has not been isolated, its existence is confirmed by the behaviour of water in benzene or acetic acid soln. of nitrogen peroxide, and by that of alcohol in benzene soln. of the peroxide. The organic nitrosates furnished by the action of nitrogen peroxide on ethylenic compounds can be regarded as derivatives of nitrosic acid.

H. Moissan and P. Lebeau found that nitrogen peroxide does not react with **fluorine** at ordinary temp. P. F. Frankland and R. C. Farmer found that chlorine is slightly soluble in the liquid peroxide. C. W. Hasenbach showed that **chlorine** has scarcely any action on well-cooled nitrogen peroxide, but if a mixture of the two gases be passed through a heated tube, presumably *chloronitric acid* is formed; **bromine** vapour and nitrogen peroxide gas when passed through a heated tube form a dark brown liquid boiling at 19°–20°, and containing 32·2–34·7 per cent. of bromine; it is thought to contain a *bromonitric acid* which is decomposed by distillation. P. F. Frankland and R. C. Farmer found bromine is miscible in all proportions with liquid nitrogen peroxide, forming a brown soln.; and **iodine** readily dissolves, forming a purple-brown soln. Iodine does not react with nitrogen peroxide under the same conditions as chlorine or bromine. P. L. Dulong said that iodine may be distilled in the gas without chemical action. A. Geuther and A. Michaelis observed that **hydrogen chloride** reacts with nitrogen peroxide, forming nitrosyl and nitroxyl chlorides. J. L. Gay Lussac said that **hydrochloric acid** furnishes nitric oxide and aqua regia. P. F. Frankland and R. C. Farmer found dry hydrogen bromide and the dry liquid peroxide are entirely without action. A. J. Balard observed that an aq. soln. of **hydrochlorous acid** gives nitric acid and chlorine. According to A. Gautier, an aq. soln. of **iodic acid** forms nitric acid and free iodine. P. F. Frankland and R. C. Farmer found that iodic acid is neither attacked nor dissolved by liquid nitrogen peroxide.

P. L. Dulong said that strongly heated **sulphur** burns in the vapour of nitrogen peroxide, but others found that the flame of burning sulphur is extinguished by the gas. P. F. Frankland and R. C. Farmer observed that sulphur is slightly soluble in the liquid peroxide without chemical action. C. Leconte found that with **hydrogen sulphide,** sulphur, water, and nitric oxide are formed; nitrogen peroxide precipitates sulphur from an aq. soln. of hydrogen sulphide and ammonia is formed. R. Weber found that if a mixture of **sulphur dioxide** and nitrogen peroxide be passed through a red-hot tube, yellow crystals of nitropyrosulphuric anhydrides are formed provided the tube is hot enough, otherwise the gases suffer no change; but at ordinary temp., C. W. Hasenbach found that they unite to form sulphuryl dinitroxyl, $SO_2.N_2O_4$, which R. Weber found is decomposed by water to form nitrosulphuric acid. W. Manchot said that at 200° to 300°, sulphur dioxide and nitrogen peroxide unite to form nitrosylsulphur trioxide, $2SO_3.NO$; and if the gases are moist nitrosylsulphuric acid is formed. F. Raschig said that in the presence of water, nitrogen peroxide does not act directly on sulphur dioxide, but rather dissolves in the water to form nitric and nitrous acids, and only the latter acts on the sulphur dioxide. L. H. Friedburg observed that nitroxylsulphonic acid is formed by the action of sulphur dioxide on a soln. of nitrogen peroxide in carbon disulphide. G. Oddo and A. Casalino found that **sulphur trioxide** reacts with nitrogen peroxide, forming **nitrosyl pyrosulphate,** $O(SO_2.O.NO)_2$. R. Weber, C. A. Winkler, C. W. Hasenbach, and L. H. Friedburg observed that **sulphuric acid** absorbs nitrogen peroxide, forming a series of substitution products (*q.v.*); G. Lunge showed that nitroxyl sulphonic and nitric acids are formed: $H_2SO_4+N_2O_4 \rightleftharpoons HNO_3+SO_2(OH)(NO_2)$; and G. Lunge and E. Weintraub further showed that the reaction is reversible. P. F. Frankland and R. C. Farmer found the liquid peroxide has at first no visible action on sulphuric acid, but in time solid nitroxylsulphonic acid is formed.

M. Berthelot observed no reaction between **nitrogen** and nitrogen peroxide. Nitrogen peroxide reacts vigorously with aq. **ammonia**; and A. Besson and G. Rosset found that liquid ammonia reacts explosively with solid nitrogen peroxide at —80°, but if a current of gaseous ammonia at —20° is passed over the peroxide, the reaction is moderated and the products are nitrogen, nitric oxide, water, ammonium nitrate, and a trace of ammonium nitrite. Nitrogen peroxide reacts slowly with ammonium chloride in the cold; the reaction is, however, complete in sealed tubes at 100° with the formation of chlorine, nitrogen, nitrous oxide, nitrogen trioxide, nitrosyl chloride, water, and nitric acid. When ammonium nitrate or sulphate replaces the chloride in the above reaction, the products are nitrogen and nitric acid or nitrogen, and a mixture of nitric and sulphuric acids respectively. For the action of nitrogen peroxide on **nitric oxide,** see Fig. 71. According to R. Weber, and G. Lunge, nitrogen peroxide is readily dissolved by dil. and conc. **nitric acid.** G. Lunge and L. Marchlewsky found that the sp. gr. of nitric acid shows a marked increase with the addition of nitrogen peroxide; and P. Pascal and M. Garnier found that the maximum occurs with a mixture containing about 42·5 per cent. by weight of the peroxide, corresponding with the compound **dinitroxydinitric acid,** $N_2O_5.N_2O_4.H_2O$, or $2HNO_3.N_2O_4$, which is stable at —48·5°, but dissociates above that temp. According to E. K. Rideal, the absorption of nitrogen peroxide by conc. nitric acid in the presence of air proceeds most rapidly at low temp., but with water, the reverse occurs. The point of inversion, that is, where absorption is independent of temp., is reached with approximately 10 per cent. nitric acid. The limitation of the nitric acid conc. to 64 per cent. in absorption towers is caused by reduction of nitric acid by the nitrogen trioxide produced. By agitation with oxygen, the N_2O_3 is converted into NO_2, and a higher conc. of nitric acid is obtained, and by cooling a 12 per cent. NO_2-air mixture to 20° to remove excess of water above that required for the equation $2N_2O_4+2H_2O+O_2=3HNO_3$, and then refrigerating to —10°, nitric acid of 61·2 to 78·1 per cent. HNO_3 was produced. W. R. Bousfield measured the sp. gr., sp. vols., v, and contractions, of mixtures of the two constituents at 4°, 14°, and 18°; and found, at 14°:

NO . .	0	8·021	26·09	37·60	43·71	48·66	51·37	96·93	100
Sp. vol. . .	0·650	0·637	0·612	0·603	0·601	0·601	0·602	0·673	0·674
Contr. . .	—	0·0032	0·0724	0·0934	0·0997	0·1011	0·1005	0·0008	—

There is a gap in the curve with between 54 and 92 per cent. nitrogen peroxide corresponding with the separation of the liquid into two layers which are mutually saturated. He found for the mutual solubilities of nitric acid in liquid nitrogen peroxide:

	Sat. soln. HNO_3 in liquid N_2O_4			Sat. soln. liquid N_2O_4 in HNO_3		
	Sp. gr.	Sp. vol.	Per cent. HNO_3	Sp. gr.	Sp. vol.	Per cent. HNO_3
4° . .	1·48742	0·67231	4·90	1·65432	0·60448	54·4
11° . .	1·47351	0·67865	6·67	1·63942	0·60997	54·3
18° . .	1·45940	0·68521	8·05	1·62501	0·61538	54·0

W. R. Bousfield also measured the temp. coeff. and found evidence of the formation of two compounds: **tetranitroxyltrinitric acid,** $3HNO_3.2N_2O_4$; and dinitroxyltetranitric acid, $4HNO_3.N_2O_4$. P. L. Dulong found that **phosphorus** continues burning in nitrogen peroxide provided it is heated more strongly than is the case with oxygen. T. Graham observed that the gas has very little action on **phosphine**; T. E. Thorpe and A. E. H. Tutton, that no combination occurs with **phosphorous oxide**; E. Tassel, that at —10° it forms white crystals of **phosphorus dinitroxylpentafluoride,** $PF_5.N_2O_4$, when treated with **phosphorus pentafluoride**; A. Geuther and A. Michaelis, that it reacts with **phosphorus trichloride** in a similar way to nitrogen trioxide, forming pyrophosphoryl, phosphoryl, and nitrosyl chlorides, phosphorus pentoxide, nitrogen, and a little nitric oxide; R. Müller, and A. Geuther that with **phosphorus pentachloride,** it forms chlorine, nitrosyl, and phosphoryl chlorides; V. Thomas, that by strongly heating nitrogen peroxide with **phosphorus triiodide,** iodine and phosphoric acid are produced. P. F. Frankland and R. C. Farmer found that **phosphoric acid** slowly absorbs some liquid nitrogen peroxide, forming a *nitroxyl phosphoric acid* insoluble in the liquid. A. Besson observed that with **antimony pentachloride, antimony dinitroxyl-pentadecachloride,** $3SbCl_5.N_2O_4$, is formed; and V. Thomas observed that with antimony trichloride, a complex is formed, and if nitrogen peroxide vapour is absorbed **antimony trichloride,** and a white complex, $Sb_4O_{11}N_2Cl_4$, is formed; complexes were also obtained with **antimony bromide,** and **antimony iodide.** A. Besson, and V. Thomas also obtained a complex with **bismuth trichloride**; and V. Thomas, one with bismuth iodide.

P. L. Dulong found that ignited **charcoal** burns in nitrogen peroxide gas with a dull red flame. C. W. Hasenbach found that at ordinary temp. **carbon monoxide** is oxidized by nitrogen peroxide, forming carbon dioxide and a volatile liquid decomposed by water. R. Müller found that at ordinary temp. **calcium carbonate** is not decomposed by nitrogen peroxide. L. H. Friedburg said that **carbon disulphide** absorbs the gas copiously. E. Turpin, and B. Setlick prepared explosives from mixtures of carbon disulphide and nitrogen peroxide. E. Turpin called his mixture *panklastite;* it could be heated to 200° without explosion, but detonated with mercury fulminate. A mixture of the vapours of carbon disulphide burns with a brilliant flame once called in commerce *selenophanite,* and when phosphorus was present, *heliophanite.*

P. F. Frankland and R. C. Farmer reported that anhydrous liquid nitrogen peroxide is inert towards numerous organic compounds, and only in exceptional cases is the reaction violent. The presence of a small quantity of water increases the chemical activity of the peroxide. As a solvent, liquid nitrogen peroxide dissolves numerous organic compounds, and in some cases the crystals of the original solute can be recovered by evaporation. The unsaturated hydrocarbons readily unite with nitrogen dioxide—thus amylene forms $NO_2.O.C_5H_9 : N.OH$—a reaction studied by E. Berl. P. F. Frankland and R. C. Farmer found that both benzene and toluene dissolve without change; naphthalene dissolves and forms dinitronaphthalene; and anthracene is oxidized to anthraquinone. The nitro-derivatives are usually very stable, thus, nitrobenzene *m-dinitrobenzene, p-nitrotoluene,* and 1 : 5-*dinitronaphthalene* are easily soluble and can be recovered from the soln. unchanged. The halogen derivatives are usually stable—thus *ethylene dibromide, acetylene tetrabromide, benzyl chloride, chlorobenzene,* and *chloroform* dissolve unchanged. J. R. Park and J. R. Partington observed no reaction with *carbon tetrachloride,* but a slight reaction with chloroform. No *carboxylic acid* was found to react while being dissolved in the menstruum. *Formic, acetic, monochloroacetic, trichloroacetic, tribromoacetic, trichlorobutyric, tartaric, and benzoic acids* readily dissolved without change, although the slightly impure peroxide reacts with tartaric and benzoic acids. The three *nitrobenzoic acids,* the three *bromobenzoic acids,* and the three *bromotoluic acids,* as well as *succinic and phthalic acids,* dissolve only with difficulty. The hydroxy-compounds are less stable towards nitrogen peroxide; thus, *ethyl alcohol* readily forms ethyl nitrite; *cane sugar* dissolves readily in the menstruum, and is attacked only if moisture be present; *phenol* reacts vigorously with the peroxide; 2 : 4-*dinitrophenol,* and *trinitrophenol* or *picric acid* dissolve readily without change; *salicylic acid* first dissolves and is then quickly attacked; while 5-*nitrosalicylic acid* dissolves slowly and is not attacked. The *ammines* are quickly attacked by liquid nitrogen peroxide, thus the three *nitroanilines,* and *β-naphthylamine* form the corresponding diazo-compounds; *pyridine* and *quinoline* are violently attacked; while neither quinine nor anthraquinone are attacked, though the former is quickly and the latter slowly dissolved. Some phases of the subject were discussed by H. Wieland, F. Guthrie, P. Pascal, etc. J. Meisenheimer, and E. de Barry Barnett studied the action of nitrogen peroxide on *anthracene* derivatives. P. Pascal found eutectics with nitrogen peroxide and 23·5 per cent. of *bromoform* at —13·5°; 91·5 per cent. of chloroform at —68°; 90 per cent. of *methyl iodide* at 69·5°; 91·85 per cent. of *carbon tetrachloride* at —49°; 86 per cent. of *phenyl bromide* at —42·5°; 92 per cent. of *chloropicrin* at —79·5°; 29·4 per cent. of *picric acid* at —13·5°; and 29 per cent. of *trinitrotoluene* at —17°. *Camphor* forms three eutectics corresponding with the formation of two compounds. According to A. Schaarschmidt, saturated aliphatic hydrocarbons are but slowly attacked by nitrogen peroxide, fatty acids being first formed and then further oxidized to oxalic acid and carbon dioxide, whilst the peroxide is reduced to nitric and nitrous oxides and ultimately to nitrogen. With olefinic hydrocarbons, however, there is immediate formation of extremely unstable isomeric nitrosates and pseudonitrosites, accompanied, in some cases, by polymerization products. Nitrogen peroxide, in the cold, converts benzene very slowly into picric acid, and toluene more readily into trinitrotoluene, as well as forming nitronitrite compounds, which are decomposed by alkalies (*e.g.* to dinitrocresol). In the presence of metallic salts (*e.g.* aluminium or ferric chlorides) benzene forms with nitrogen peroxide complex additive compounds which are decomposed by water. A. Schaarschmidt found that saturated aliphatic hydrocarbons are but slowly attacked by nitrogen peroxide, fatty acids being first formed and then further oxidized to oxalic acid and carbon dioxide, whilst the peroxide is reduced to nitric and nitrous oxides and ultimately to nitrogen. Branched-chain paraffins are less resistant than straight-chain paraffins. When the reaction occurred in a closed glass tube, there was no evolution of heat, but, even after the appearance of nitrogen trioxide in the tube, the mixture cooled as soon as the source of the external heat was removed. With olefinic hydrocarbons (*e.g.* amylene, cyclohexene), there is immediate formation of extremely unstable isomeric nitrosates and ψ-nitrosites, accompanied, in some cases, by polymerization products. Nitrogen peroxide, in the cold, converts benzene very slowly into picric acid, and toluene more readily into trinitrotoluene. At the same time, nitro-nitrite compounds are formed, which are decomposed by alkalies (*e.g.* to dinitrocresol). A. Schaarschmidt and E. Smolla attributed the explosives, which have been known to occur in nitrogen fixation plants, to the action of nitrogen peroxide on the olefinic constituents of benzene. E. Berl did not agree with this.

The adsorption of nitrogen peroxide by the hydrogel of **silica** has been studied by P. C. Ray, J. A. Almquist and co-workers, and C. M. Faber and co-workers. N. W. Krase proposed to use silicagel for separating nitrogen peroxide from the gases obtained in the oxidation of ammonia. Liquid nitrogen peroxide can be transported in steel containers, and it is a more convenient form for transporting nitric nitrogen than is nitric acid. A. Geuther found that **boron trichloride** forms oxide and **boron nitrosyltetrachloride,** $BCl_3.NOCl$; and P. F. Frankland and R. C. Farmer showed that liquid nitrogen peroxide neither attacks nor dissolves **boric acid.**

According to P. L. Dulong, **potassium** takes fire in the vapour of nitrogen peroxide at ordinary temp., and burns with a red flame; **sodium** also decomposes the vapour without disengaging heat or light; **copper** acts on the vapour slowly at ordinary temp., and rapidly when heated, forming copper oxide and nitric oxide. P. Sabatier and J. B. Senderens observed that finely divided copper in the cold absorbs nitrogen peroxide—freed from all traces of nitric acid—forming what they called *cuivre nitré*. *Nitrocopper* was represented by the formula Cu_2NO_2, and considered to be a chemical compound. Its properties were described, but these are all characteristic of the properties of nitrogen peroxides. H. V. Tartar and W. L. Semon showed that the alleged compound is not formed by the action of nitrogen peroxide on copper, and they consider that the product is a film of anhydrous cuprous nitrate on the surface of copper. J. R. Park and J. R. Partington measured the rate of absorption of nitrogen peroxide by copper, and showed that the first action probably involves the formation of cuprous oxide with the evolution of heat, $2Cu+NO_2=Cu_2O+NO$; the cuprous oxide then absorbs nitrogen peroxide up to the saturation point—33 per cent. nitrogen peroxide. On heating, the gas is given off and cuprous oxide remains; the gas is re-adsorbed on cooling. The nitrogen peroxide can be all removed by carbon tetrachloride at 65°–70°. The alleged nitrocopper is therefore an adsorption complex of nitrogen peroxide in cuprous oxide. A. Klemenc and A. Schroth confirmed this conclusion, saying that the *Nitrokupfer und wahrscheinlich auch die anderen Nitrometalle sind als chemische Verbindungen aus der Literatur zu streichen.* E. Divers and T. Shimidzu poured liquid nitrogen peroxide on reduced copper and observed a brisk effervescence with the evolution of nitric oxide, and the formation of what was thought to be cuprous nitrate mixed with cupric nitrate. R. Müller showed that at $-10°$, liquid nitrogen reacts with many **metals,** forming the metal nitrate and nitric oxide; the latter uniting with the excess of nitrogen peroxide forms the trioxide. P. Sabatier and J. B. Senderens found that finely divided **silver** reacts with nitrogen peroxide, forming nitric oxide and silver nitrate; copper under similar conditions gives cuprous nitrate. They found that **magnesium** filings burn vigorously when heated to dull redness in an atm. of nitrogen peroxide; and **zinc** at about 300° forms zinc oxide. P. L. Dulong observed that **mercury** is slowly attacked by the vapour of nitrogen peroxide, while E. Divers and T. Shimidzu found that the liquid reacts with mercury, forming a mixture of mercurous and mercuric nitrates. The reaction was studied by W. A. Noyes. P. Sabatier and J. B. Senderens said that **aluminium** filings are not perceptibly attacked by the gas at 500°. P. L. Dulong observed that **tin** is slowly attacked by nitrogen peroxide at ordinary temp.; and P. Sabatier and J. B. Senderens, that at about 200°, **lead** forms a basic nitrate. According to A. Guntz, pyrophoric **manganese** inflames in the gas; but the non-pyrophoric metal reacts at a suitable temp. thereby forming a mixture of manganese oxides, while a trace of nitrite is simultaneously produced. P. L. Dulong observed that **iron** is slowly attacked by nitrogen peroxide at a red-heat, forming ferric oxide, and nitric oxide; P. Sabatier and J. B. Senderens said that the reaction with reduced iron begins at about 350°; reduced **cobalt** at a suitable temp. burns in the gas, forming cobaltosic oxide; and reduced **nickel,** at 250°, forms nickel monoxide. It was also found that the finely divided metals in the cold absorb nitrogen peroxide, forming *nitro-iron*, Fe_2NO_2; *nitrocobalt*, Co_2NO_2; and *nitronickel*, Ni_4NO_2. The observations made above on the nitrocopper are almost certain to be valid also for these substances.

P. L. Dulong reported that when the vapour of nitrogen peroxide is passed over **barium oxide** at ordinary temp., the gas is absorbed; at 200°, the baryta suddenly becomes red-hot and fuses, forming a mixture of nitrite and nitrate. J. R. Partington and F. A. Williams found that nitrogen peroxide reacts with **calcium oxide** at all temp. up to 400°, giving primarily calcium nitrite and nitrate. Secondary reactions, however, occur at higher temperatures; above 230°, calcium nitrite decomposes, $Ca(NO_2)_2=CaO+NO+NO_2$, and in the presence of nitrogen peroxide undergoes oxidation at lower temp. in the following ways: (1) $Ca(NO_2)_2+2NO_2=Ca(NO_3)_2+2NO$, (ii) $Ca(NO_2)_2+NO_2\rightarrow Ca(NO_3)_2+0{\cdot}5N_2$. At 450°, the mol. proportions of the decomposition are represented by $12{\cdot}02$ mols. $Ca(NO_2)_2\rightarrow 7{\cdot}68CaO+4{\cdot}34Ca(NO_3)_2+14{\cdot}40NO+N$, nitrogen and nitric oxide alone being evolved. Above 480°, nitrogen peroxide is, in addition, given off, and at 495° calcium nitrate begins to decompose. I. Guareschi found that **soda-lime** or **potash-lime** readily absorbs nitrogen peroxide at ordinary temp. R. Müller said that in general the liquid peroxide reacts with the **metal oxides,** forming the metal nitrate and nitrogen trioxide. A. Klemenc and A. Schroth found that the adsorption of nitrogen peroxide by a mixture of copper and **cuprous oxide** is less at higher than at lower press. They found the absorption equilibrium, with cuprous oxide:

	0°	11·5°	20°	26°	30°	40°
$p_{NO_2-N_2O_4}$.	0·338	0·620	0·900	1·15	1·35	2·27 atm.
NO_2 per cent. .	1·41	3·24	4·08	—	5·27	5·11

If *a* c.c. of nitrogen peroxide are absorbed per gram at 0° and 760 mm., when the press is *p* atm., at 40°:

p . . .	0·338	0·620	0·900	1·15	1·35	2·27 atm.
a . . .	6·8	15·6	19·6	23·8	25·9	24·5

The results plotted on a smoothed curve in Fig. 88, show that the adsorption isotherm passes through a maximum at about 1·6 atm. press. P. Sabatier and J. B. Senderens found that black cuprous oxide reacts at 300°, forming cupric oxide; **stannous oxide** forms stannic oxide; **lead oxide,** a basic nitrate; **titanium sesquioxide,** white titanic oxide; **vanadium trioxide,** the brown pentoxide; **tungsten dioxide,** yellow tungstic oxide; **manganous oxide,** manganese sesquioxide; and **uranium dioxide,** a basic nitrate. D. Tommasi found that with a boiling soln. of **potassium dichromate,** a complex *potassium chromochromate,* $[(CrO_2)_3(CrO_3)_2K_2O]H_2O$, is formed. The *potassium nitrodichromate* or *potassium nitroxyldichromate,* $KO.Cr_2O_5.NO_2$, of L. Darmstädter could not be prepared by G. C. Schmidt, and G. N. Wyrouboff.

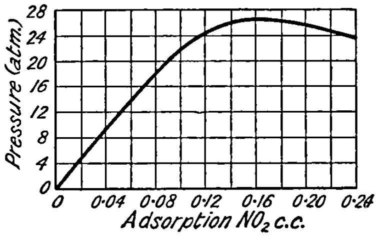
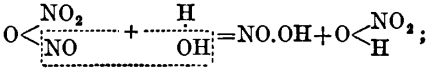


FIG. 88.—Adsorption Isotherm for Cuprous Oxide and Nitrogen Peroxide at 40°.

P. F. Frankland and R. C. Farmer observed no case in which an inorganic salt was dissolved by liquid nitrogen peroxide, provided the liquid is purified. If moisture be present, many chlorides are attacked rather quickly. The **alkali chlorides and fluorides** are not attacked by the dried liquid, but if moisture be present, **potassium chloride** is attacked and chlorine is set free to be dissolved by the liquid; **potassium bromide and iodide** are attacked by the dry or moist liquid, setting free the halogen. The liquid peroxide does not dissolve or attack **potassium nitrate, sulphate,** or **chlorate,** and the same remark applies to **sodium nitrite,** and **hydrazine sulphate.** V. Thomas prepared addition compounds of nitrogen peroxide with **copper chloride,** and **copper bromide**; E. Luck, one with **magnesium phosphate** and nitrogen peroxide; V. Thomas, with **zinc chloride, zinc bromide, zinc iodide, cadmium chloride, cadmium bromide,** and **cadmium iodide.** V. Thomas described a complex $SnOCl_2.3SnCl_4.N_2O_5$, or $Sn(NO_3)_2Cl_2.3SnCl_4$, *stannic nitratochloride* as a product of the action of nitrogen peroxide on a dil. chloroform soln. of stannic chloride. P. F. Frankland and R. C. Farmer found that **mercuric nitrate,** and **cyanide** are neither dissolved nor attacked by liquid nitrogen peroxide. A. Besson obtained a complex with **aluminium chloride.** If nitrogen peroxide acts for a short time on **titanic chloride,** unstable *titanic nitroxyl chloride,* $2TiCl_4.3N_2O_4$, is formed; with a more prolonged action titanic nitrate, $Ti(NO_3)_4$, is produced. V. Thomas obtained complexes with **stannic chloride,** and **stannic bromide.** H. Reihlen and A. Hake found that when a soln. of nitrogen peroxide in carbon disulphide acts on an excess of stannic chloride, at 0°, brown *stannic nitroxyl chloride,* $3SnCl_4.2NO_2$, is formed; it decomposes on warming. If an excess of nitrogen peroxide is used, at $-60°$, yellow $2SnCl_4.3N_2O_4$ is formed; and if nitrogen trioxide acts on stannic chloride, $3SnCl_4.4NO_2$ is formed. V. Thomas prepared complexes with **lead chloride, lead bromide,** and **lead iodide**; E. Späth, with **uranyl nitrate,** namely, **uranyl dinitrosylnitrate,** $UrO_2(NO_3)_3(NO_2)_2$. P. F. Frankland and R. C. Farmer found that **iron acetonylacetone,** $Fe(C_6H_9O_2)_3$, and **iron benzylacetone,** $Fe(C_{10}H_9O_2)_3$, were quickly attacked by the liquid peroxide, but no iron passed into soln.; **ferric chloride** was not attacked by the dry liquid, but if moisture be present, the salt is attacked and iron passes into soln. F. Besson, and V. Thomas obtained complex salts with ferric chloride; and V. Thomas, with **ferric bromide.** M. Berthelot passed **nickel carbonyl** into liquid nitrogen peroxide, or mixed the vapours of the two compounds and obtained a blue vapour.

The constitution of nitrogen peroxide.—The analyses of J. L. Gay Lussac,[6] P. L. Dulong, and E. Péligot agree with the empirical formula NO_2, and, as indicated above, the density of the gas shows that there are two forms of the oxide N_2O_4 predominating at low temp., and NO_2 at higher temp. The constitution is doubtful. J. Priestley, C. L. Berthollet, H. Davy, and T. Thomson considered that nitrogen peroxide is a combination of nitric acid with nitric oxide, and not a direct combination of oxygen with nitrogen because (i) nitric oxide converts nitric acid into nitrogen peroxide; and (ii) nitrogen peroxide is decomposed by water into nitric acid and nitric oxide—they did not take into account the intermediate formation of nitrous acid. There are several possibilities for the structure of the low temp. form, thus, it may be regarded as *nitrosyl nitrite*, $O:N.O.NO_2$; *dinitroxyl*, $O_2N.NO_2$; or as *nitrosyl dioxide*, $ON.O.O.NO$. The evidence is very indecisive. A. Exner argued in favour of $O:N.O.NO_2$ because of the reaction $NO_2Cl+AgNO_2=AgCl+N_2O_4$; and also because of its decomposition by water into nitrous and nitric acids, $NO.O.NO_2+H.OH=NO.OH+NO_2.OH$, or by alkali-lye into alkali nitrite and nitrate



$$O<^{NO_2}_{NO} + {}^{H}_{OH} = NO.OH + O<^{NO_2}_{H};$$

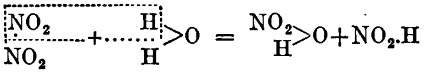
L. Henry, because of the production of alkyl nitrates and iodine when nitrogen peroxide acts on the alkyl iodides; A. C. Girard and J. A. Pabst, because of its formation from potassium nitrate and nitroxylsulphuric acid: $NO_2HSO_3+KNO_3=N_2O_4+KHSO_4$; O. N. Witt, because of the formation of diazobenzolnitrate and water by the action of nitrogen peroxide on aniline: $NO_2.O.NO+C_6H_5.NH_2=C_6H_5:N_2O.NO$; and H. Reihlen and A. Hake, because it forms a complex with stannic chloride,

$$Cl_4Sn\left[O:N.O.N<^{O}_{O}>SnCl_4\right]_2, \quad \text{not} \quad Cl_4Sn\left[<^{O}_{O}>N-N<^{O}_{O}>SnCl_4\right]$$

which it would do if it had the symmetrical structure $O_2N.NO_2$. This hypothesis would relate the three higher oxides of nitrogen:

$$\underset{N_2O_3}{NO.O.NO} \qquad \underset{N_2O_4}{NO_2.O.NO} \qquad \underset{N_2O_5}{NO_2.O.NO_2}$$

R. Günsberg, and E. Müller favoured the second formula $O_2N.NO_2$, because of the reaction of nitrogen peroxide with water which he represented:



$${}^{NO_2}_{NO_2} + {}^{H}_{H}>O = {}^{NO_2}_{H}>O+NO_2.H$$

H. Wieland added that while the conception of nitrogen peroxide as a mixed anhydride of nitrous and nitric acids $O=N-O-NO_2$ is in harmony with its action on alkali-lye, yet a similar conception for nitrogen trioxide, $ON.O.NO$, is not in harmony with the blue colour assumed to be in accord with the tinctorial qualities of a nitroso-derivative, $ON.NO_2$. The corresponding formula $O_2N.NO_2$ is in harmony with many of its reactions; its dissociation by heat; and the action of water and alkali-lye which is analogous to that of the other symmetrically paired atoms or radicles—*e.g.* cyanogen to cyanide and cyanate; and chlorine to chloride and hypochlorite. For G. Oddo's view of the structure, *vide supra*, hydrated nitrogen peroxide. J. C. Thomlinson assumed the oxygen atoms to be quinquevalent in order to explain the thermochemical data. V. Meyer considered that the third formula, $ON.O.O.NO$, is in keeping with the union of amylene and nitrogen peroxide to form $C_5H_{10}(NO_2)_2$, which by reduction gives ammonia, showing that the carbon is not directly attached to the nitrogen, but to oxygen. This gives the formula $ON.O.C_5H_{10}.O.NO$. E. Divers, and J. J. Sudborough and J. H. Millar also regarded nitrogen peroxide as a nitrosyl peroxide. G. Kirsch, and H. Henstock discussed the electronic structure.

The dissociation product NO_2 behaves in many respects as a univalent radicle with one free valency. O. Piloty and B. G. Schwerin consider the nitrogen atom is quinquevalent, $O=N=O$, or may be tervalent, ${}^{O}_{O}>N-$. L. Spiegel favoured the former hypothesis; E. Divers, and J. J. Sudborough and J. H. Millar, tervalent $O=N-N-$. A. Schaarschmidt considers that the various ways nitrogen peroxide can react with organic compounds—*vide supra*—favour the assumption that it occurs as an equilibrium mixture of the three forms:

$$\begin{array}{l} O\text{—}N{=}O \\ \dot{O}.N{=}O \end{array} \rightleftharpoons \begin{array}{l} O{=}\underset{\cdot}{N}{=}O \\ \quad\ \dot{O}\text{—}N{=}O \end{array} \rightleftharpoons \begin{array}{l} O{=}N{=}O \\ O{=}\dot{N}{=}O \end{array}$$

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§ 40. Nitrogen Pentoxide

In 1840, H. St. C. Deville[1] discovered that **nitrogen pentoxide,** N_2O_5, or **nitric anhydride** is formed when dried chlorine is passed over dried silver nitrate contained in a U-tube, heated on a water-bath. The reaction begins at 95°, and then proceeds regularly at 60°. The pentoxide can be collected as a colourless solid in a bulb-tube surrounded by a freezing mixture. The reaction is symbolized $4AgNO_3+2Cl_2=4AgCl+2N_2O_5+O_2$. M. Odet and L. Vignon added that it is advisable to eliminate all joints of rubber or cork from the apparatus, and to connect the glass parts of the apparatus by fused or ground-in points, or else by placing one tube inside the other and filling in the intermediate space with asbestos and paraffin. M. Odet and L. Vignon assumed that in the reaction between chlorine and silver nitrate, nitroxyl chloride is formed as an intermediate product, $AgNO_3+Cl_2=AgCl+NO_2Cl+O$; and they obtained the pentoxide by passing nitroxyl vapour over silver nitrate at 60° to 70°, and collecting the products of the reaction in a cooled vessel: $AgNO_3+NO_2Cl=N_2O_5+AgCl$. C. Weltzien found that if iodine is used in place of chlorine, silver iodide and iodate, and nitrogen peroxide are formed. D. Helbig made nitrogen pentoxide by the action of ozone on nitrogen peroxide; and the reaction was studied by F. Förster and M. Koch, and F. Daniels, O. R. Wulf, and S. Karrer. The results show that one mol. of ozone is required to oxidize one mol. of nitrogen tetroxide at 25°; thus only one atom of the ozone mol. is available in the oxidation at this temp. This result is in striking contrast to the oxidation of sulphur dioxide to the trioxide by ozone at temp. below 40°, in which one mol. of ozone oxidizes three mols. of sulphur dioxide, all three atoms of the ozone mol. being available for oxidation. According to F. O. Anderegg and co-workers, the fog formed when ozonized air is passed through an absorbent soln. is due chiefly to hygroscopic nitrogen pentoxide. The yields of ozone and nitrogen pentoxide in air are much more dependent on the nature and extent of the surface than on the amount of inductive capacity of the various materials placed in the discharge space. Glass wool is particularly active. An increase of voltage is accompanied by an increased formation of ozone, followed by that of nitrogen pentoxide, a high conc. of which lowers the yield of ozone. Thus the conc. of the latter reaches a first, second, and sometimes a third maximum. H. Fischer observed that some nitrogen pentoxide and ozone are formed when Tesla currents of 25,000 volts pass through mixtures of oxygen and nitrogen.

Nitrogen pentoxide is most conveniently made from anhydrous nitric acid which is obtained by the repeated distillation of a mixture of conc. sulphuric and nitric acids. The nitrous acid is removed by passing dry air through the nitric acid. The acid is cooled in a beaker, and phosphorus pentoxide added gradually with constant stirring, while the temp. is kept as low as possible. The addition of phosphorus pentoxide is continued until further additions produce but a small rise of temp. The cold, syrupy liquid is then added to a cooled retort, which is then gently heated, when an orange distillate collects in the receiver surrounded by cold water. On standing, the liquid distillate separates into two layers. The upper layer is decanted into a thin-walled tube, and cooled by iced water when crystals of the pentoxide soon separate out. The orange-coloured liquid is poured off, and the crystals are melted at as low a temp. as practicable ; the liquid is cooled and the mother-liquid again poured away from the crystals. J. Giersbach and A. Kessler said that if the nitric acid employed is free from water, it mixes with phosphorus pentoxide quietly without hissing. The yield with R. Weber's process is small. M. Berthelot obtained a 60–70 per cent. yield by working as follows :

> Rather more than its own weight of phosphoric anhydride is added in small quantities at a time to nitric acid, HNO_3, cooled in a freezing mixture so as to avoid any considerable rise in the temperature, which should not at any time be above zero. The pasty mass thus obtained is then rapidly transferred to a tubulated retort capable of containing 5 or 6 times the quantity, and distilled very slowly, collecting the product in stoppered bottles surrounded with ice. The anhydride condenses in long, transparent, colourless crystals which, when exposed to the air, slowly evaporate without deliquescing.

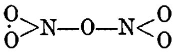
The process of R. Weber was also modified by L. Meyer, G. E. Gibson, and F. Daniels and A. C. Bright. According to F. Russ and J. Pokorny, the operation is facilitated by passing dry ozonized oxygen through the system during the distillation. This prevents the decomposition of the pentoxide into oxygen and the lower oxide of nitrogen. They also used solid carbon dioxide as the refrigerating agent. Some irregularities in the physical properties of ozone led V. H. Veley and J. J. Manley to the conclusion that 100 per cent. nitric acid is a mixture of nitric acid, HNO_3, nitrogen pentoxide, and water.

According to H. St. C. Deville, nitrogen pentoxide furnishes transparent, colourless, prismatic crystals of great brilliancy ; and, according to F. Daniels and A. C. Bright, they are hexagonal prisms, and grow several millimetres in length on standing for a long time at 0°. H. St. C. Deville found that when slowly deposited in a current of strongly cooled gas, the crystals attain considerable size. R. Weber said that molten nitrogen pentoxide is readily undercooled, and the liquid has a darker colour than when solid. J. B. A. Dumas found that the liquid obtained by melting the crystals in a sealed glass tube may explode when the tube is immersed in a freezing mixture. R. Weber found the sp. gr. of the crystals to be about 1·6 ; M. Berthelot, 1·63. I. I. Saslavsky discussed the mol. vol. H. St. C. Deville gave 29°–30° for the m.p. ; R. Weber, about 30° ; and M. Berthelot, 29·5°. F. Russ and J. Pokorny, and F. Daniels and A. C. Bright found that the m.p. lies above the sublimation point, and the observations on the m.p. must have been made with pentoxide contaminated with atm. moisture. The colour of the solid darkens when the temp. is raised, and the crystals become yellow just before melting, and the colour at the m.p. is orange. The colour becomes dark brown as the temp. rises, and at about 45°, the liquid boils with decomposition into nitrogen peroxide and oxygen. H. St. C. Deville said that the vap. press. at 10° is considerable; the measurements of the vap. press. p mm. by F. Russ and J. Pokorny below 10·5°, and of F. Daniels and A. C. Bright above that temp., are as follow:

	−33°	−21°	−10·7°	0°	10·5°	15°	25°	30°	32·5°
p . .	2·3	6·3	18·6	51·5	132	183	420	620	760

F. Russ and J. Pokorny found their results could be represented by $\log p = -3161{\cdot}2T^{-1}+1{\cdot}75 \log T - 0{\cdot}00606T + 10{\cdot}679$; and F. Daniels and A. C. Bright, by $\log p = 1244T^{-1}+34{\cdot}1 \log T - 85{\cdot}929$ mm. The calculated mol. heat of fusion is —8·28 Cals., and the mol. heat of sublimation, —4·84 Cals. The heats of sublimation calculated from the vap. press. are 12·36 Cals. at —10°; 12·76 Cals. at 0°; 13·36 Cals. at 10°; 14·14 Cals. at 20°; and 14·97 Cals. at 32·5°. M. Berthelot obtained 13·10 Cals. at 10°; he also gave for the heat of formation, $(N_2,5O) = -1{\cdot}2$ Cals. for the gas; $(N_2,5O)=3{\cdot}6$ Cals. for the liquid; $(N_2,5O)=11{\cdot}8$ Cals. for the solid; and $(N_2,5O)=28{\cdot}6$ Cals. for the heat of soln. J. Thomsen gave $(N_2,5O)=29{\cdot}82$ Cals.; $(N_2,5O,Aq.)=47{\cdot}56$ Cals.; $(2NO,3O,Aq.)=72{\cdot}97$ Cals.; $(N_2O_3,Aq.,O)=36{\cdot}64$ Cals.; $(2NO_2,O,Aq.)=33{\cdot}83$ Cals.; $(N_2,5O,H_2O)=14{\cdot}66$ Cals.; $(N_2O,4O,H_2O)=32{\cdot}4$ Cals.; $(2NO,3O,H_2O)=57{\cdot}81$ Cals.; and $(2NO_2,O_2,H_2O) = 18{\cdot}67$ Cals. J. C. Thomlinson calculated what he called the thermochemical eq. of oxygen in nitrogen pentoxide. F. Daniels found that the dissolution of nitrogen pentoxide in organic liquids—*e.g.* chloroform or dichloroethane—causes the absorption maxima of the bands of the ultra-red to shift from 5·65μ to 5·45–5·30μ. The results do not support the radiation hypothesis of chemical action. It is assumed that the relative position of the electron pair between the atoms of a molecule determines the ultra-red absorption spectra.

The analysis of H. St. C. Deville corresponds with the formula N_2O_5. The probable assumption that the contained nitrogen is quinquevalent agrees with the formula $O_2{\equiv}N{-}O{-}N{\equiv}O_2$. It can thus be regarded as *nitroxyl oxide*, $(NO_2)_2O$. L. Spiegel added that if the nitrogen atoms were tervalent, and the oxygen atoms bivalent, the graphic formula would be $O{=}N{-}O{-}O{-}O{-}N{=}O$; or



$$\genfrac{}{}{0pt}{}{O}{O}{>}N{-}O{-}N{<}\genfrac{}{}{0pt}{}{O}{O}$$

C. D. Niven, and H. Henstock discussed the electronic structure.

H. St. C. Deville said that if the temp. does not exceed 8°, the crystals can be kept for a month in diffuse daylight without decomposition; at 25°, in sunlight, the salt melts and decomposes explosively into nitrogen peroxide and oxygen. R. Weber kept the crystals for several days at 10° without any very marked decomposition. M. Berthelot said that the pentoxide decomposes rapidly when exposed to the direct rays of the sun, and it is not explosive either in the solid or gaseous state, but since it decomposes into nitrogen peroxide and oxygen at ordinary temp., it should not be kept in sealed tubes, but rather in stoppered bottles. F. Daniels and E. H. Johnston studied the thermal decomposition of nitrogen pentoxide between 0° and 65°, and the velocity constant, K, was found to have the values:

	0°	15°	20°	25°	35°	45°	55°	65°
K . .	$0{\cdot}0_4472$	$0{\cdot}0_3624$	0·00117	0·00203	0·00808	0·0299	0·0900	0·292

The decomposition at all temp. appears to be unimolecular. The large temp. coeff. of the reaction velocity shows that catalysis by the glass walls and diffusion are not factors in the reaction. The system studied was really $2N_2O_5 \rightarrow (2N_2O_4 \rightleftharpoons 4NO_2)+O_2$. M. Bodenstein regards the thermal decomposition as a purely unimolecular reaction, $N_2O_5 \rightarrow N_2O_3+O_2$. F. Daniels and co-workers found that a trace of ozone retards the thermal decomposition of the pentoxide. The reaction was discussed by M. Bodenstein. H. S. Hirst found that the thermal decomposition of nitrogen pentoxide is a true unimolecular reaction. The temp. coeff. of the velocity is large, being 300 per cent. for 10° rise of temp. so that the reaction is not a wall-effect. The decomposition at 80° is almost instantaneous. According to W. F. Busse and F. Daniels, the rate of the thermal decomposition of nitrogen pentoxide is not affected by the presence of bromine, chlorine, carbon monoxide or hydrogen; carbon disulphide gives an increase in the rate of decomposition. When ethyl ether is added to decomposing nitrogen pentoxide, a decrease in press. is produced, and then a rapid increase.

According to H. S. Hirst, the critical increment, E, in the photochemical equation (**4.** 25, 8) is 24,700 cals., and the rays of wave-length $1{\cdot}16\mu$ should be photochemically active; but they are not. Light in the region $400\mu\mu$ to $460\mu\mu$ accelerates the decomposition, but this does not occur unless nitrogen peroxide is present. The autocatalytic effect of nitrogen peroxide is negligible in the dark. F. Daniels said that the photochemical decomposition of the pentoxide is not brought about by the ultra-red radiation; the slight decomposition observed at 25° is a thermal effect produced by the radiation, since at 0°, where the thermal decomposition is negligible, no decomposition occurs. At least 99·5 per cent. of the absorbed radiation is chemically inactive. It is inferred that absorptions in the ultra-red and ultra-violet have fundamentally different mechanisms. H. A. Taylor believed that nitrogen pentoxide is not decomposed by the absorption of 3 or 5 quanta of energy at 3·39 or $5{\cdot}81\mu$, at which wave-lengths this oxide possesses strong absorption bands. S. C. Roy studied the photochemical reaction from the point of view of the radiation hypothesis. R. H. Lueck found that the velocity constants in chloroform or carbon tetrachloride soln. at 25° and 55° approximate closely to those obtained by F. Daniels and co-workers. The energy of activation or critical increment is nearly independent of temp. The nitrogen peroxide formed in the reaction acts as an autocatalyst on the decomposition of the pentoxide. E. C. White and R. C. Tolman observed no evidence of autocatalysis in their study of the rate of decomposition of nitrogen pentoxide. H. S. Hirst and E. K. Rideal found that the surface of the containing vessel, or the presence of inert gases, or the presence of the products of the reaction do not disturb the unimolecular character of the thermal decomposition of nitrogen pentoxide. The high value of the heat of activation, *viz.* 24,700 cals. per mol, precludes the possibility of the energy of activation being supplied by inelastic thermal collisions, or by black-body radiation unless some chain mechanism is called into play. The decomposition is not retarded by reducing the press., but below a critical press. of about 0·25 mm., the velocity of the reaction increases, becoming, at 0·01 mm. press., approximately constant, and five times its normal value. This is considered to be irreconcilable with chain mechanism—such, for instance, as the passage of a radiation quantum through a chain of successive mols., each one re-emitting the quantum after reaction; or else by the production by the decomposition of an activated form of nitrogen dioxide which, on collision, causes further reaction. It is therefore supposed that a definite fraction of the activated mols. always undergoes decomposition irrespective of press., but that a larger fraction (about four-fifths) does not decompose if it collides within 10^{-6} sec. after activation, but is deactivated by collision. A possible explanation of the two different types of activated mols. is based on the fact that there are four NO linkings, and only one shared NO linking in the mol. of the pentoxide. Activation of one linking causes decomposition, activation of the shared linking invariably so; activation of the others, only after a time interval and if collisions do not intervene. J. J. Thomson, J. A. Christiansen, J. A. Christiansen and H. A. Kramers, G. N. Lewis and D. F. Smith, and R. C. Tolman and co-workers, discussed the theory of this reaction; and Y. K. Sirkin showed that the quantum theory—**4.** 25, 8—can be adapted to the decomposition of nitrogen pentoxide. C. S. Fazel and S. Karrer found that nitrogen pentoxide, in the presence of nitrogen peroxide, is decomposed by light. It is assumed that the chemical activity of the NO_2-mols. is excited by the absorption of blue light; but R. G. W. Norrish suggested that since nitrogen peroxide is decomposed by the light of a mercury lamp: $2NO_2=2NO+O_2$, the reaction proceeds: $NO+N_2O_5=3NO_2$. According to W. F. Busse and F. Daniels, the photochemical decomposition of nitrogen pentoxide in the presence of the photocatalyst nitrogen peroxide is not affected by the presence of oxygen, nitrogen, or hydrogen; bromine cannot be substituted for nitrogen peroxide in the photochemical decomposition of nitrogen pentoxide even though its absorption spectrum is similar, in fact, bromine decreases the catalytic efficiency of nitrogen peroxide, probably by screening out the effective light. A. K. Brewer noted that ionization occurs during the decomposition of the pentoxide at 385°.

F. W. Küster and S. Münch could not obtain molten nitrogen pentoxide without it showing a pale yellow colour. T. Soné gave $-0{\cdot}03\times10^{-6}$ mass units for the magnetic susceptibility of the solid pentoxide. H. St. C. Deville said that the pentoxide deliquesces rapidly in air, and dissolves in water with the evolution of much heat, but no gas, forming a colourless soln. of nitric acid, HNO_3. R. Weber found that when the pentoxide is in contact with sulphur, it gives off brown vapours and forms a white sublimate approximating $SO_3.N_2O_3$, *sulphatonitrous anhydride*; A. Pictet and G. Karl said that the pentoxide dissolves in freshly distilled and fused sulphur trioxide, forming *sulphatonitric anhydride*, $(SO_3)_4.N_2O_5$, or $O(SO_2.O.SO_2.O.ON_2)_2$. W. F. Busse and F. Daniels observed that nitric oxide reacts immediately with nitrogen pentoxide. R. Weber found that nitrogen pentoxide has no action on carbon, but in the vapour of the pentoxide carbon burns with as brilliant a light as in oxygen; potassium and sodium burn brilliantly in the gas; magnesium, zinc, and cadmium are slightly attacked; and the metals—copper, silver, aluminium, thallium, titanium, tin, lead, antimony, bismuth, tellurium, iron, nickel, and palladium—are passive towards the pentoxide; but arsenic, and mercury are vigorously oxidized. It reacts on many organic substances with great vigour—thus, it explodes in contact with naphthalene. G. E. Gibson recommended it as a nitrating agent.

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§ 41. Nitric Acid—History and Occurrence

The alchemical writings between the twelfth and fifteenth centuries have been searched by the scholars for indications of a knowledge of the mineral acids. If saltpetre was not recognized as a chemical individual prior to the thirteenth century, nitric acid is not likely to have been made before that time. An ill-founded attempt has been made to trace the discovery of nitric acid to the ancient Egyptians. W. Herapath[1] inferred that some linen cloth marked with dark hieroglyphical characters indicated that the Egyptians, at the time of Moses, were acquainted with nitric and hydrochloric acids. Since the ashes of the cloth were found to contain silver, it was assumed that the markings were produced by silver nitrate. J. D. Smith said that W. Herapath's assumption is wholly gratuitous, since there are other means of getting silver into soln. without the intervention of any acid whatever. T. J. Herapath also showed that a chemical analysis of the markings is of no value.

According to H. Kopp,[2] the earliest known description of a method of making nitric acid appears in the twelfth-century Latin work *De inventione veritatis*, attributed to the eighth-century Arabian Geber. It says:

> Take a pound of Cyprus vitriol, a pound and a half of saltpetre, and a quarter of a pound of alum. Submit the whole to distillation in order to withdraw a liquor which has a high solvent action. The dissolving power of the acid is greatly augmented if it be mixed with some sal ammoniac, for it will then dissolve gold, silver, and sulphur.

The distillation of vitriol, alum, and saltpetre would provide nitric acid; and the addition of sal ammoniac would furnish aqua regia. A somewhat similar mode of making the acid is described in the *Compositum de compositis* attributed to the twelfth-century Albertus Magnus. Similarly in the *Testamentum novissimum*, attributed to the thirteenth-century Raymond Lully, the acid was prepared by distilling a mixture of saltpetre and clay. A description of these methods of making nitric acid was copied into other writings during the immediately succeeding centuries. Thus, it appeared in Agricola's *De re metallica* (Basilæ, 1546); in N. Lemery's *Cours de chimie* (Paris, 1675); and in J. R. Glauber's *Furnis novis philosophicis* (Amstelodami, 1648), the acid is said to be obtained by heating saltpetre with vitriol, or alum, or clay, or white arsenic. J. Kunckel, in his *Philosophia chemica experimentis confirmata* (Amstelodami, 1694), recommended the white arsenic process. As H. Boerhaave said in his *Elementa chemiæ* (Lugduni Batavorum, 1732): Joannes Rudolphus Glauberus was "the first of mortals" to prepare this acid by the action of sulphuric acid on saltpetre. J. R. Glauber[3] wrote:

> I know well that ignorant laborators which do all their work according to custom, without diving any further into the nature of things, will count me a heretic because I teach that the *aqua fortis* made of vitriol and saltpetre is of the same nature and condition as the *spiritus nitri* which is made without vitriol.

In his *Miraculum mundi* (Franckfurt, 1658), J. R. Glauber acutely added:

> Plainly after the very manner we have taught spirit of salt to be prepared, so may also *aqua fortis* be made. Instead of salt, take saltpetre, and you will have *aqua fortis*.

His detailed description of the preparation of nitric acid, by the action of sulphuric acid on nitre, is written in the absurdly quaint style of the older alchemists;

First a man is to be made of iron, having two noses on his head, Fig. 89, and on his crown a mouth which may be opened and again close shut. This if it be to be used for the conc. of metals is to be so inserted into another man made of iron or stone, that the inward head only may come forth of the outward man, but the rest of his body or belly may remain hidden in the belly of the exterior man. And to each nose of the head glass receivers are to be applied to receive the vapours ascending from the hot stomach. When you use this man you must render him bloody with fire to make him hungry and greedy of food. When he grows extremely hungry he is to be fed with a white swan. When that food shall be given to this iron man, an admirable water will ascend from his fiercy stomach into his head, and thence by his two noses flow into the appointed receivers; a water, I say, which will be a true and efficacious aqua-vitæ; for the iron man consumeth the whole swan by digesting it, and changeth it into a most excellent and profitable food for the king and queen, by which they are corroborated, augmented, and grow. But before the swan yieldeth up her spirit she singeth her swan-like song, which being ended, her breath expireth with a strong wind, and leaveth her roasted body for meat for the king, but her *anima* or spirit she consecrateth to the gods that thence may be made a salamander, a wholesome medicament for men and women.

FIG. 89.—The Iron Man with Two Noses.

The term commonly employed for nitric acid in the translations of Geber's writings is *aqua dissolutiva*, and less frequently, *aqua fortis;* Albertus Magnus called the acid *aqua prima*, and *aqua dissolutiva;* Raymond Lully, *aqua fortis, aqua acuta*, or *aqua calcinativa*; and G. Agricola (*De re metallica*, Basiliæ, 1546), *aqua valens*. V. Biringucci (*Pirotechnica*, Venezia, 1540), G. Agricola, and books on assaying which began to appear in the sixteenth century, describe the use of *Starkwasser* (nitric acid) in the inquartation of gold. B. Budé, in his *De asse et partibus ejus* (Paris, 1516), called it *chrysulca*—from χρυσός, gold; and ἕλκω, draw out—and also *eau de départ;* while Basil Valentine, in his *Offenbahrung der verborgenen Handgriffe* (Erfurth, 1624), called the acid *Scheidewasser*—in allusion to its use for parting gold and silver. J. R. Glauber called the acid made from saltpetre and sulphuric acid *spiritus acidus nitri;* and that made from saltpetre and alum, *aqua fortis*. The acid distilled from a mixture of saltpetre and sulphuric acid was often alluded to during the sixteenth and seventeenth centuries as *spiritus nitri fumans Glauberi*. H. Boerhaave called it *acidum nitri*, and during the next forty years, it was often termed *acide nitreux* or *nitrous acid*. O. Guttmann[4] described its manufacture in Birmingham in 1771. In the nomenclature recommended in 1787 by the French chemists, it received its present cognomen *acide nitrique*, or *nitric acid*.

About 1750, G. F. Rouelle[5] described an ingenious process for concentrating nitric acid—or, as he called it, *l'esprit de nitre ou acide nitreux*—by distilling a mixture of the dil. nitric acid with conc. sulphuric acid. J. Mayow,[6] in 1669, showed that saltpetre consists of an alkali salt and a salt of a volatile acid, which is expelled as *spirit of nitre* when saltpetre is treated with sulphuric acid. Spirit of nitre was also shown to be a compound of what he called nitro-aerial spirit with particles of a grosser nature. The nitro-aerial particles were supposed to be derived from the air, and to be necessary for the production of the flame. The clear advance made by J. Mayow on the nature of *spiritus nitri* seems to have been overlooked because during the next century the ideas of chemists on the nature of nitric acid seem to have undergone a process of involution; progress was backwards not forwards.

In 1734, G. E. Stahl propounded the hypothesis that like sulphurous acid, nitric acid is a compound of sulphuric acid and phlogiston, but the proportions of phlogiston in the two acids are different. In 1750, J. G. Pietsch wrote a thesis in support of this view; but in 1786, P. Thouvenal showed that while nitric acid is produced by the putrefaction of organic matter, sulphuric acid is never so formed. G. A. Saluzzo considered nitric acid to be a compound of an empyreumatic acid, an alkaline salt, lime, and a little silica; and T. Bergman regarded it as a dephlogisticated plant acid produced by fermentation.

In 1776, A. L. Lavoisier demonstrated the presence of oxygen in nitric acid, and this discovery recalls J. Mayow's nitro-aerial particles; in 1784, H. Cavendish synthesized it by the action of electric sparks in humid air, and proved that it contained oxygen and nitrogen; and in 1816, J. L. Gay Lussac, and C. L. Berthollet established its exact composition.

According to F. Goppelsröder,[7] free nitric acid does not occur in nature although A. Emmerling claimed to have observed it in plants where it was supposed to have been formed by the decomposition of calcium or alkali nitrates in plants by oxalic acid. On the other hand, several nitrates—ammonium, potassium, sodium, magnesium, aluminium, and iron—have been reported in numerous localities. There are, for instance, the nitre deposits near the west coast of South America, and the soil of Amu-Daria, Turkestan, found by N. Ljubawin to contain about 3 per ccnt. of nitrates. The presence of nitrates and nitrites in the atmosphere has been previously discussed in connection with atm. air (*q.v.*). In 1695, B. Ramazzini detected the presence of nitric acid in snow; and in 1751, A. S. Marggraf observed the acid in rain-water, and in snow. This subject has been discussed in connection with nitrous acid, atmospheric air, and the fixation of nitrogen by bacteria. A. S. Marggraf, H. Cavendish, and T. Bergman detected nitrates in spring waters. Nitrates have been detected in numerous forms of running water, particularly those carrying drainage waters from soils. W. Knop, C. Ekin, C. H. John, F. Goppelsröder, J. von Liebig, C. F. Schönbein, T. Schlösing, J. B. J. D. Boussingault, A. Müntz, V. Marcano and A. Müntz, A. Lévy, R. Otto and J. Troeger, C. H. John, etc., have discussed the occurrence of nitrates in natural waters—rivers, and oceans. The presence of nitrates has been reported in various organs of plants, and the nitrates appear to be connected with the assimilation of nitrogen by plants. The subject has been discussed by F. Goppelsröder, F. Schulze, A. Hosaeus, C. Ekin, M. Berthelot, M. Berthelot and G. André, V. Dessaignes, W. Knop, M. Serno, M. Vaudin, etc. The occurrence of nitrates in animals—urine, sweat, saliva, etc.—has been discussed by C. F. Schönbein, F. Goppelsröder, C. Wurster, T. Weyl, F. Röhmann, etc. According to H. B. Jones, nitrates are formed in the animal system by the oxidation of nitrogenous matters by the oxygen dissolved in the blood.

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§ 42. Nitric Acid—Preparation

The production of nitric acid by the oxidation of nitrogen, either in the electric arc, or during the simultaneous oxidation of other substances, has been previously discussed in connection with the fixation of nitrogen. Nitric acid is the end-product of the oxidation of nitric oxide, and of nitrogen trioxide or peroxide ; and this subject has been discussed in connection with the individual compounds. S. Cloez and E. Guignet[1] and others have studied the oxidation of ammonium salts, and of nitrogenous organic matter to nitrates by digestion with potassium permanganate, and other oxidizing agents—*vide* the oxidation of ammonia. The nitrification of organic matter in soils, etc., to nitrates by bacteria has been discussed in connection with the fixation of nitrogen.

When potassium or sodium nitrate is mixed with dil. sulphuric acid in the cold, no obtrusive sign of chemical action occurs, although it can be proved that a reversible change has taken place so that the sodium is distributed between the sulphuric and nitric acids. The same mixture is obtained whether the original constituents are sulphuric acid and sodium nitrate or sodium hydrosulphate and nitric acid. The one reaction is endo- and the other exo-thermal. If a mixture of conc. sulphuric acid and sodium nitrate be heated to about 130°, nitric acid, HNO_3, is volatilized. The reaction is represented : $NaNO_3+H_2SO_4\rightleftharpoons NaHSO_4+HNO_3$. The two salts, sodium nitrate and sodium hydrosulphate, are not volatile ; the nitric acid, HNO_3, boils at 86° ; and the sulphuric acid at 330°. Hence, on warming to 100° in a retort, most of the nitric acid is volatilized and the state of equilibrium of the soln. is disturbed ; in consequence, the sodium nitrate is all decomposed. If the oily liquid in the retort be cooled, a little unchanged nitrate may be deposited along with the crystals approximating $NaH_3(SO_4)_3$. At 121°, the crystals are almost wholly sodium hydrosulphate. At a still higher temp., normal sodium sulphate is formed and hence less sulphuric acid is needed for a given yield of nitric acid: $2NaNO_3+H_2SO_4=Na_2SO_4+2HNO_3$. Appreciable quantities of the nitric acid are decomposed at the higher temp. Brownish-red fumes appear when the mixture is first heated, and the distillate is more or less coloured brown because of the soln. of the ruddy gas in the distillate. The brownish-red gas is a product of the decomposition of the nitric acid by heat; as represented by L. Carius,[2] $4HNO_3=2H_2O+4NO_2+O_2$. According to C. W. Cuno, if the reduction in the yield of nitric acid is due in part to this reaction brought about by the dehydrating action of sulphuric acid, the introduction of an excess of air or oxygen should lessen the loss. In fact, the brown fumes in the distillation can be nearly prevented in this way; the amount of oxygen required for the purpose increasing with the temp. of distillation.

If the proportions of sulphuric acid and sodium nitrate approximate $2NaNO_3+H_2SO_4=Na_2SO_4+2HNO_3$, the temp. required to complete the action is high—nearly 900°, and this results in heavy wear and tear on the apparatus; high fuel consumption; much loss by the thermal decomposition of the nitric acid; and the residual sulphate is difficult to remove from the retort. By sacrificing a portion of the sulphuric acid, and working more nearly to the equation: $NaNO_3+H_2SO_4=NaHSO_4+HNO_3$, the temp. need not exceed 200°, and the residue in the retort can be allowed to run from the retort. Rather less acid than that corresponding with this equation is employed in practice so that the residue is a mixture of sodium hydrosulphate and sulphate. It is known as *nitre-cake.* The composition and properties of nitre-cake have been discussed by H. W. Foote, H. M. Dawson, B. Saxton, and G. S. Butler and H. B. Dunnicliff. Trials with different proportions of acid and nitrate have been reported by G. C. Wittstein, N. A. E. Millon, E. Mitscherlich, R. Phillips, C. F. Bucholz, H. Hess, and P. L. Geiger. The early workers preferred potassium nitrate for making the acid on a small scale because that salt could be more easily purified than the sodium salt—Chili saltpetre.

The salts employed for making nitric acid should be as free as possible from halogen salts. Ordinary Chili saltpetre contains some iodine, and the resulting acid, as shown by M. Lembert,[3] and E. A. White, may contain this impurity. According to W. Stein, the iodine may be present in its elemental form or as iodine chloride. If the salts contain chlorides, the product may be contaminated with hydrochloric acid, or chlorine or nitrosyl chloride. For special purposes, the dil. acid may be treated with silver nitrate, and the clear liquor, free from silver chloride, redistilled for nitric acid. If any silver chloride is present in the retort, it will be partly decomposed by the hot acid. This subject was discussed by H. W. F. Wackenroder, F. Mohr, G. C. Wittstein, and E. Ohlert. J. Bescherer recommended distilling the acid over metallic silver, but the remedy is not effective. Lead oxide is inefficacious because some lead chloride dissolves in the nitric acid and is decomposed by heat. Commonly, the chlorides are volatilized early and collect in the first fraction, so that by rejecting the first third of the distillate, L. C. A. Barreswil, and N. A. E. Millon obtained an acid free from this impurity. P. Pascal, and J. Baumann studied the fractional distillation of nitric acid. R. Hirsch described a continnous process of rectifying nitric acid from the more volatile constituents. E. and R. Urbain described a rectifier in which water was extracted from the vapour by atmolysis through porcelain, and they thus made 99·6 per cent. nitric acid. H. J. M. Creighton showed that when nitric acid is electrolyzed in a cell with a porous diaphragm separating anode and cathode, the acid is concentrated by the electrolytic decomposition of water, and the concentration of the acid in the anolyte is increased at the expense of the catholyte, by the migration of the NO_3'-ions. He thus raised the conc. of 70–71 per cent. acid to 99·65 per cent. HNO_3. A. Erck added methyl or ethyl alcohol, before rectification, whereby he claimed that the halogen impurities and organic substances are volatilized more readily, and collected in the first fraction. The traces of sulphuric acid or sodium sulphate mechanically carried over from the vapours can be removed by redistillation which may or may not be preceded by treatment with barium nitrate to precipitate the sulphates. V. H. Veley and J. J. Manley obtained an acid of a high degree of purity by distilling, under reduced press., ordinary conc. acid mixed with small proportions of silver and barium nitrates to remove chlorides and sulphates respectively. The yellow or yellowish-red colour of the acid due to the presence of nitrogen peroxide was removed by N. A. E. Millon by heating the acid to near the b.p.—say 80° or 90°—and passing in a current of carbon dioxide until the acid is cold. H. E. Roscoe used air instead of carbon dioxide; and V. H. Veley and J. J. Manley, a stream of ozonized oxygen to remove the lower nitrogen oxides, and distilled the product under reduced press. N. A. E. Millon recommended distilling the acid with about a hundredth part of its weight of potassium dichromate; and J. Pelouze, lead or barium dioxides. This subject was further discussed by L. C. A. Barreswil, H. W. F. Wackenroder, F. Mohr, C. G. Wittstein, E. Ohlert, and O. Guttmann. W. G. Whitman and L. Evans found that the removal of the lower oxides of nitrogen from nitric acid by a current of air follows the equation $-dC/dt=\beta C$, where C denotes the conc. of the nitrogen oxides, and β is a constant depending on the temp. and rate of flow of air. H. N. Warren found traces of selenious acid in a sample of commercial nitric acid. This impurity was probably derived from the sulphuric acid. F. A. F. Crawford examined the organic impurities in nitric acid; G. Lockemann, arsenic.

The purification and concentration of the acid can be effected by fractional distillation in a current of inert gas, or ozonized oxygen whereby 98 per cent. HNO_3 can be obtained; and, by the low temp. redistillation of the conc. acid with its own vol. of conc. sulphuric acid, H. E. Roscoe obtained an acid of 99·5–99·8 per cent. HNO_3. The concentration of the acid by the fractional distillation of the acid with or without the addition of sulphuric acid was discussed by J. Pelouze, J. Dalton, J. Tünnermann, H. J. M. Creighton and co-workers, M. Kaltenbach, F. Förster and co-workers, E. Galle, C. D. Carpenter and J. Babor, E. Mitscherlich, G. Lunge and H. Rey, R. Weber, J. L. Gay Lussac, J. L. Proust, A. Smith, N. A. E. Millon, D. P. Konowaloff, and J. Giersbach and A. Kessler. The acid can be concentrated by freezing. According to F. W. Küster and S. Münch, when nitric acid containing 98·5 per cent. of HNO_3 is partially frozen, and the liquid removed, almost pure nitric acid is obtained. By continued fractionation, products were obtained of constant f.p., that is, the temp. at which successive fractions began to crystallize were constant. As solidification, however, proceeded, the temp. fell appreciably, and this indicated that an impurity was present which could not be removed by fractional crystallization. The acid obtained in this manner contained 99·4±0·1 per cent. of HNO_3. Absolute nitric acid exists only in the form of snow-white crystals at a temp. below −41°. Nitric acid crystals melt to a yellow liquid, which is a soln. of nitrogen pentoxide and water in nitric acid. Whilst solid nitrogen pentoxide is colourless, the liquid has not yet been obtained colourless. This liquid, in presence of dry air, becomes colourless, the pentoxide being removed and the water remaining. The liquid obtained after removal of the pentoxide contained 98·67 per cent. of HNO_3. When dry air was passed into an acid containing 99·4 per cent. of HNO_3, the yellow colour of the acid disappeared exactly at the point when the percentage of HNO_3 was 98·67. J. Giersbach and A. Kessler obtained 100 per cent. nitric acid by mixing nitrogen pentoxide with the calculated quantity of water, but this acid is partly dissociated $2HNO_3 \rightleftharpoons N_2O_5+H_2O$.

Instead of decomposing the nitrate with sulphuric acid, the early workers employed vitriol, alum, clay, or white arsenic as indicated in the preceding section. T. Ramon de Luna[4] employed magnesium sulphate; R. Wagner, aluminium hydroxide, and precipitated silica; and F. Kuhlmann, manganese chloride, sulphate, or dioxide. W. Garroway treated a mixture of an alkaline earth and the alkali nitrate with steam; G. Lunge and M. Lyte likewise treated a mixture of the alkali nitrate and ferric oxide. The process was described in detail by J. L. F. Vogel. J. D. Darling and C. L. Forrest electrolyzed the molten nitrate for the alkali metal, and passed the resulting gases into water.

F. Förster and co-workers [5] found that the concentration of nitric acid above 68 to 69 per cent. HNO_3, by treatment of dil. nitric acid with nitrogen peroxide, water, and oxygen, may be effected if the time of treatment is extended, the oxygen used only in slight excess, and the gas velocity reduced. Even so, only 80 per cent. nitric acid is produced. A very high conc. results by interaction of the weak nitric acid soln. with sufficient excess of liquid nitrogen peroxide, followed by slight agitation with oxygen. When the equilibrium $2NO_2 \rightleftharpoons N_2O_4$ is reached in the treatment of nitrous gases with water, nitric peroxide dissolves, and thereby initiates the interaction $N_2O_4+H_2O \rightleftharpoons HNO_3+HNO_2$, the nitrous acid being then decomposed into nitric acid and nitric oxide, and oxidized.

Nitric acid is manufactured at the present day by one of three processes: (i) By the direct oxidation of nitrogen in the electric arc as indicated in connection with the fixation of nitrogen; (ii) By oxidation of ammonia as indicated in connection with that compound; and (iii) By the decomposition of sodium nitrate with sulphuric acid. Some chemical changes involved in the third reaction have just been discussed. The plant employed consists of (i) the distilling apparatus; (ii) the condensing system; (iii) the receiving vessel; (iv) the bleaching system; and (v) the absorption apparatus.

The retorts formerly employed were made of glass or iron; they are now made of cast iron. The older retorts were cylindrical and were supported horizontally in the flue of the fire; the more modern retorts are of the pot-type, and are supported vertically in the flue. There are several modifications of the pot retort—*e.g.* by O. Guttmann,[6] F. Valentiner, J. Prentice, etc. That of J. Prentice has a loose bottom which can be cemented in as required. F. Bottomley recommended retorts of fused silica. The condensing apparatus formerly employed consisted of a battery of Woufile's bottles cooled by air; but both air and water are now usually employed. There are several different systems of condensation—*e.g.* those of O. Guttmann, E. Hart, A. Hough, J. V. Skoglund, etc. The receiving apparatus for the condensed acid can be made of well-vitrified stoneware, glass, fused silica, and acid-resisting alloys. Formerly acid was decolorized by blowing a current of air through the warm product. In J. V. Skoglund's bleaching system, the hot condensed acid is allowed to reflux so as to meet the hot gases from the retort which raise its temp. and drive out the nitrogen peroxide, or all but about one per cent. of nitric acid. From 6 to 10 per cent. of the nitrogen content of the original nitrate passes the condenser and receiver. This is recovered by passing the gases through a series of absorption towers packed with acid-proof material, and down which trickles dil. nitric acid. The gas with the most nitrous fumes comes in contact with the most conc. acid, while the gas almost freed from nitrous fumes comes in contact with the most dil. acid. C. L. Burdick and E. S. Freed found that the reactions in the absorption towers involve the reversible reaction: $3NO_2+H_2O \rightleftharpoons 2HNO_3+NO$; and the reaction: $2NO+O_2=2NO_2$ which goes to an end, but is comparatively slow. The slowness of the reaction and the necessarily limited capacity of the towers prevent complete recovery—a 95 per cent. conversion being considered good practice.

There are many modifications—*e.g.* in F. Valentiner's process in which the decomposition of the nitrate is carried out under reduced press., and accordingly at a reduced temp., so as to avoid thermal decomposition of the nitric acid. This process was modified by H. Fischer, and A. Hough. According to W. Mason, the best results are obtained with the press. reduced from 25 to 15 mm. of mercury. The formation of nitrous acid, which is especially to be avoided in this process, is unconnected with the use of an iron pot but is caused by over-heating; with careful firing, even with sulphuric acid of sp. gr. 1·75, the nitrous acid content may be as low as 0·2 per cent. An undesirable acceleration of the distillation accompanied by frothing often occurs, when about 30 per cent. of the nitric acid distillation has occurred, is due to the loss of water from the acid sulphate. A yield of 97–99 per cent. nitric acid is obtained by this method. There are also continuous systems of manufacturing nitric acid by M. Prentice, C. Uebel, etc. Manufacturing details of these and other technical processes are described in A. Cottrell's *The Manufacture of Nitric Acid and Nitrates* (London, 1923). There are also numerous articles in the technical journals.[7]

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§ 43. The Composition of Nitric Acid and its Hydrates

According to V. H. Veley and J. J. Manley,[1] and F. W. Küster and S. Münch, absolute nitric acid exists only in snow-white crystals stable below —41°; on melting it partly decomposes into water and nitrogen pentoxide which dissolves in the melted acid to form a yellow soln. When a current of dry air is passed through the liquid, the liberated nitrogen pentoxide escapes, and a colourless acid containing 98·67 per cent. of HNO_3 results. This acid can be volatilized unchanged. E. Aston and W. Ramsay said that the 99·8 per cent. acid has a pale yellow colour, and fumes strongly when exposed to air. The commercial nitric acids contain different proportions of water, and vary in colour from a pale straw-yellow to an orange-brown owing to the presence of the lower nitrogen oxides in soln.

The red fuming liquid known as **fuming nitric acid** is a soln. containing a variable quantity of nitrogen peroxide in conc. nitric acid. It is produced by introducing nitrous acid, nitric oxide, or nitrogen trioxide or peroxide, into conc. nitric acid. E. Mitscherlich said that monohydrated nitric acid can dissolve half its weight of nitrogen peroxide. The fuming acid is made by distilling a mixture of sodium or potassium nitrate with half its weight of sulphuric acid, with fuming sulphuric acid, or with potassium hydrosulphate. In any case the reaction: $KHSO_4+KNO_3=K_2SO_4+HNO_3$, occurs at so high a temp. that the nitric acid is decomposed, forming nitrogen peroxide, which dissolves in the distillate; with the conc. sulphuric acid, some nitrogen pentoxide is formed, and this also dissolves in the distillate. C. Brunner, and E. Schaller recommended making the fuming acid by adding either sulphur or starch to the mixture of alkali nitrate and sulphuric acid in the retort. L. Vanino made the fuming acid by adding paraformaldehyde to conc. nitric acid. Many other organic substances can be used.

The fuming acid was very early recognized to be a soln. of nitrogen trioxide and peroxide in nitric acid. L. Marchlewsky said some nitric oxide is present, but showed that N_2O_4 and NO_2 are the dominant solutes. D. Gernez, and L. Marchlewsky argued that a labile compound of nitric acid and nitrogen peroxide is present because (i) a very marked contraction occurs when these two constituents are mixed together—Table XXXI shows the results of G. Lunge and L. Marchlewsky's observations on the effect of nitrogen peroxide on the density of nitric acid; and (ii) a soln. of nitrogen peroxide in chloroform, benzene, or carbon disulphide shows the nitrogen peroxide spectrum, while the soln. in conc. nitric acid

TABLE XXXI.—EFFECT OF NITROGEN PEROXIDE ON THE SPECIFIC GRAVITY OF NITRIC ACID.

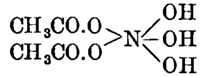
(Sp. gr. of acid 1·4960 at 15°/4°.)

N_2O_4 per cent.	Rise in specific gravity.			
	0·00	0·25	0·5	0·75
0	—	0·0050	0·00075	0·00150
1	0·00300	0·00475	0·00675	0·00775
2	0·01050	0·01250	0·01425	0·01625
3	0·01800	0·01985	0·02165	0·02350
4	0·02525	0·02690	0·02875	0·03050
5	0·03225	0·03365	0·03600	0·03775
6	0·03950	0·04175	0·04300	0·04475
7	0·04650	0·04720	0·05000	0·01565
8	0·05325	0·05500	0·05660	0·05825
9	0·06000	0·06160	0·06325	0·06500
10	0·06600	0·06815	0·06975	0·07135
11	0·07300	0·07450	0·07600	0·07750
12	0·07850	0·08050	0·08210	0·08350

does not. C. Montemartini argued against chemical combination because nitrogen peroxide can be extracted from the fuming acid by carbon disulphide. The maximum density of mixtures of nitrogen peroxide and nitric acid was found by G. Lunge and L. Marchlewsky to be a maximum with 42·5 per cent. of the peroxide. This corresponds with **nitroxyl nitric acid,** $2HNO_3.N_2O_4$, or $HNO_3.NO_2$. W. R. Bousfield obtained singular points in the sp. vol. curve corresponding with $4HNO_3.N_2O_4$, and $3HNO_3.2N_2O_4$. In their study of the reciprocal solubility of nitric acid and nitrogen proxide, P. Pascal and M. Garner found this complex acid to be stable below −48·5° and above this temp. to dissociate giving off the peroxide. They also found that sulphuric acid is not appreciably soluble in nitrogen peroxide, but when added to anhydrous nitric acid or the acid containing a little water, it does not appreciably alter the solubility of the peroxide in the acid providing the mixture does not contain more than 30 per cent. of sulphuric acid, the water content being the principal factor of solubility.

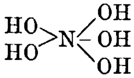
Red fuming nitric acid is highly corrosive. According to S. Feldhaus, if water be slowly added to the acid, the colour changes from dark red to brown and yellowish-green, and, with ice-cold water, a dil. soln. is blue. When warmed, the soln. gives off nitric oxide. No gas is evolved if the acid be added to water slowly enough to prevent a rise of temp. L. Marchlewsky and co-workers said that the blue soln. contains only nitrous acid, the green soln. nitrous acid and nitrogen peroxide. When the red, fuming acid gives off nitrogen peroxide and a colourless hydrate remains, its sp. gr. is 1·5, and L. Carius found that it oxidizes organic compounds to carbon dioxide any sulphur present being converted to sulphuric acid, and any phosphorus into phosphoric acid; he therefore recommended it for use as an oxidizing agent in organic analysis. Fuming nitric acid is a more powerful oxidizing agent than nitric acid alone; it inflames phosphine, hydrogen selenide, hydrogen iodide, straw, saw-dust, and other organic substances. These reactions were discussed by L. Archbutt, R. Haas, A. W. Hofmann, K. Kraut, G. Lechartier, and K. Lund. Some of its general properties are those of nitric acid, others of nitrogen peroxide.

Many investigations on the physical properties of soln. of nitric acid showed the existence of discontinuities which have been interpreted to mean that definite hydrates are formed. This was noted by E. A. Smith[2] in 1848. E. A. Bourgoin, E. Mitscherlich, A. Bineau, M. Berthelot, H. Erdmann, W. N. Hartley, T. Graham, J. Kolb, and J. Wislicenus also suggested that nitric acid forms definite hydrates. V. H. Veley and J. J. Manley, and S. U. Pickering observed discontinuities in the f.p. curve corresponding with the existence of a monohydrate and a trihydrate; M. Berthelot, J. Thomsen, and S. U. Pickering observed corresponding sharp breaks in the heat of soln.; C. Chéneveau, in the viscosity curves; W. N. Hartley, in the absorption spectra; H. Crompton, and V. H. Veley and J. J. Manley, in the electrical conductivity or resistance curves; and V. H. Veley and J. J. Manley in the curve of refractive indices. The curves showed singularities corresponding with hydrates with 14, 7, 4, 3, 1½, and 1 H_2O. H. Erdmann claimed to have isolated by freezing at low temp. hydrates with 2, 1½, 1, and ½ H_2O. If dry air be passed through nitric acid at −15°, water evaporates and *orthonitric acid*, $HNO_3.2H_2O$, or $N(OH)_5$, remains. This hydrate is stable at −15°, and furnishes long needles which melt at −35°, and the liquid boils at 40°–40·5°, and 13 mm. press. By treating nitric acid (sp. gr. 1·4) with acetic anhydride, $(CH_3CO)_2O$, the fraction which boils at 127·7° (730 mm.) has a sp. gr. 1·197 (15°). Its empirical formula is $C_4H_9NO_7$ and its general properties, mol. wt., and mode of preparation show that it is a mixed anhydride—**diacetylorthonitric acid**—with the constitutional formula:



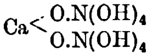
$$\begin{array}{l}CH_3CO.O\\CH_3CO.O\end{array}{>}N\begin{array}{l}/OH\\-OH\\\backslash OH\end{array}$$

Diacetylorthonitric acid, $(CH_3COO)_2N(OH)_3$.



$$\begin{array}{l}HO\\HO\end{array}{>}N\begin{array}{l}/OH\\-OH\\\backslash OH\end{array}$$

Orthonitric acid, $N(OH)_5$.



$$Ca{<}\begin{array}{l}O.N(OH)_4\\O.N(OH)_4\end{array}$$

Calcium nitrate, $Ca(NO_3)_2.4H_2O$.

While orthonitric acid itself is unstable, this compound is comparatively stable, and it can be distilled without decomposition. Crystallized calcium nitrate, $Ca(NO_3)_2.4H_2O$, can be considered to be the calcium salt of orthonitric acid. The constitution of nitric acid was discussed by A. Hantzsch. H. Erdmann said that he had obtained prismatic crystals of *pyromesonitric acid,* $2HNO_3.3H_2O$, or $H_8N_2O_9$, or $(HO)_4N.O.N(OH)_4$, which freezes at —39° ; rhombic plates of *mesonitric acid,* $HNO_3.H_2O$, or H_3NO_4, or $O : N(OH)_3$, which freezes at —34° ; and stellar aggregates of *pyrometanitric acid,* $2HNO_3.H_2O$, or $H_4N_2O_7$, or $(OH)_2NO.N.O.NO(OH)_2$, which freezes at —65·2°, and boils at 21·5° and 24 mm. press. The corresponding *metanitric acid* would be represented by HNO_3, or $(HO)NO_2$, ordinary nitric acid. There is but little satisfactory evidence of the polybasicity of these acids, although G. Oddo showed the higher oxygenated compounds of nitrogen may have a tendency to form complexes by polymerization, because the acid salt $KNO_3.HNO_3$ may be regarded as a monopotassium salt of *dinitric acid ;* and $KNO_3.2HNO_3$, as the monopotassium salt of *trinitric acid :*

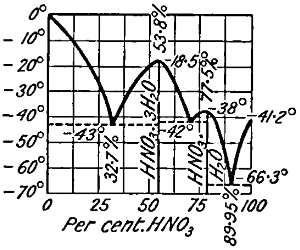
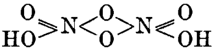
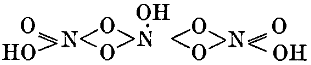


FIG. 90.—Fusion Curves of the Binary System : $HNO_3–H_2O$.



$$\mathrm{{}^{O}_{HO}{>}N{<}{}^{O}_{O}{>}N{<}{}^{O}_{OH}}$$

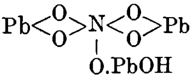
Dinitric acid, $H_2N_2O_6$.



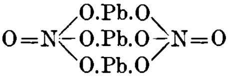
$$\mathrm{{}^{O}_{HO}{>}N{<}{}^{O}_{O}{>}\overset{OH}{\dot{N}}{<}{}^{O}_{O}{>}N{<}{}^{O}_{OH}}$$

Trinitric acid, $H_3N_3O_9$.

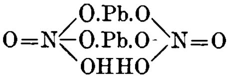
A number of basic lead salts have been considered as salts of some of these acids. Thus, J. Loewe referred the salt $6PbO.N_2O_5.H_2O$ to orthonitric acid, and $3PbO.N_2O_5$ to metanitric acid ; and J. J. Berzelius, and M. E. Chevreul also referred the salt $2PbO.N_2O_5.H_2O$ to metanitric acid :



$6PbO.N_2O_5.H_2O$.



$3PbO.N_2O_5$.



$2PbO.N_2O_5.H_2O$.

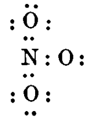
H. L. Wells, and H. Klinger's basic nitrates of lead, cadmium, zinc, and mercury were shown by G. Watson to fall in line with this hypothesis ; but F. Meissner could not support it, and F. W. Kuster and R. Kremann showed that the f.p. curve of binary mixtures of nitric acid and water invalidates H. Erdmann's conclusions—*vide infra.*

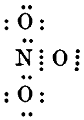
In 1786, H. Cavendish measured the f.p. of mixtures of nitric acid and water, and he showed that when the liquid is frozen, it exhibits two kinds of congelation. What he called *spiritous congelation* occurs when the more conc. acid is frozen, and with a more dil. acid *aqueous congelation.* Translated into modern language, in the one case nitric acid first freezes out of soln., and in the other case ice. He also obtained what he called a *point of easiest freezing* at —1·5°. This point nearly a century later was called the eutectic temp. J. Dalton obtained a buttery mass by cooling the acid to —54°, and M. Berthelot froze the conc. acid to a solid at —47°. F. W. Küster and R. Kremann examined the f.p. of binary mixtures: $HNO_3–H_2O$, in some detail. The results are summarized in Fig. 87. The ice-curve falls down from zero to the first eutectic with 32·7 per cent. of HNO_3 at —43·0° when the two solid phases are ice and **trihydrated nitric acid,** $NHO_3.3H_2O$. The curve rises from this eutectic to a maximum at —18·5° and 53·80 per cent. of HNO_3, corresponding with the m.p. of the trihydrate. There is then a fall to a second eutectic at —42·0° with 70·50 per cent. of HNO_3. The two solid phases are the trihydrate, and **monohydrated nitric acid,** $HNO_3.H_2O$. The curve then rises to a second maximum at —38·0° and 77·75 per cent. HNO_3 corresponding with the m.p. of the monohydrate. The curve then falls to a third eutectic at —66·3° and 89·95 per cent. HNO_3. The two solid phases are the monohydrate and nitric acid, The curve then rises to —41·2, the m.p. of 100 per cent. HNO_3. These two hydrates were first isolated by S. U. Pickering, who gave —18° for the m.p. of the trihydrate, and —36·8 for that of the monohydrate. V. H. Veley and J. J. Manley gave respectively —18·2° and —45°. Irregularities with 96–100 per cent. HNO_3, are connected with anhydride formation. H. Crompton found that the second differential of the electrical conductivity curves agreed with the assumption that the two hydrates, $HNO_3.4H_2O$, and $HNO_3.15H_2O$, are formed in accord with the breaks in the first differential of D. I. Mendeléeff's sp. gr. curves—*vide* sulphuric acid. Observations were also made by C. D. Carpenter and A. Lehrman.

Analyses of nitric acid by A. L. Lavoisier, H. Cavendish, J. J. Berzelius, H. Davy, and H. St. C. Deville agree with the empirical formula HNO_3. The calculated value for the **vapour density** is 31·5. L. Playfair and J. A. Wanklyn obtained 2·375 for the vap. density at 40·5°, and 2·258 at 68·5°, but A. Calm showed that the vapour density of the acid cannot be determined because of dissociation. Nitric acid is nearly always regarded as being constituted with quinquevalent nitrogen, but I. I. Kanonnikoff inferred that the indices of refraction of a number of nitrates agreed better with tervalent nitrogen. These two hypotheses are symbolized:

$$HO{-}N\leqslant^{O}_{O} \qquad\qquad HO{-}N<^{O}_{O}.$$

J. W. Brühl's observations on the refractive indices agreed with the formula $HO.O.N{=}O$; but R. Löwenherz's values for ethyl, propyl, isobutyl, and amyl nitrates agree better with the quinquevalent nitrogen atom. H. E. Armstrong and F. P. Worley made some observations on the constitution of nitric acid—*vide* sulphuric acid. H. Burgarth, H. Remy, and H. Henstock discussed the electronic structure; and from observations on the absorption spectra of sodium and potassium nitrates in different solvents, G. Scheibe inferred that the nitrate ion is dipolar, and that the electronic structure is such that the first of the following forms exists in equilibrium with small proportion of the second:





G. Oddo and G. Anelli found that in what are usually regard as associating solvents—nitrobenzene, and in ethylene bromide—the cryoscopic data give values for the mol. wt. which are only slightly larger than is required for HNO_3. An analogous result was obtained by F. M. Raoult with acetic acid, and by E. Mameli with chloroacetic acid. N. Tschernay concluded from his observations on the coeff. of thermal expansion of soln. of the nitrates that nitric acid exists in soln. with doubled molecules $(HNO_3)_2$, or $H_2N_2O_6$; and E. Aston and W. Ramsay found the mol. wt. is nearly 126, the theoretical value for $H_2N_2O_6$, 63, corresponding with a mixture of $H_2N_2O_6$-mols. with a small proportion of HNO_3-mols. W. N. Hartley also inferred from his observations on the absorption spectra that the molecules in aq. soln. are complex $(HNO_3)_n$, and in some cases form the equivalent of mesonitric acid, H_3NO_4. He believed that the hypothesis is supported by the observations of W. H. Perkin, S. U. Pickering, and V. H. Veley and J. J. Manley; and said that the anhydrous acid is probably bi-molecular, $H_2N_2O_6$; and with acids between 78 and 100 per cent. HNO_3 there is a mixture of mesonitric acid, H_3NO_4, and the bi-molecular acid, $H_2N_2O_6$. The former is supposed to be active, the latter inert.

According to A. Hantzsch, while in aq. soln., nitric acid behaves as if it were constituted $HO.NO_2$, in alcoholic soln., the hydrogen can be split off by electrolytic dissociation. The optical properties also indicate that under these conditions the constitution may alter to $NO_3.H$. He calls the latter a *pseudo-acid*, meaning an acid which is homopolar with respect to hydrogen, but whose hydrogen atoms do not exercise an acid function, which, in the case of oxy-acids, are linked with oxygen in the form of hydroxyl. When water is added, the pseudo-acid becomes a true acid by a change in its constitution and optical properties. D. D. Karve found that the heats of soln. of nitric acid in alcohol and ether support the hypothesis. A. Hantzsch and L. Wolf assume that soln. of nitric acid contain equilibrium mixtures of the pseudo-acid, $HO.NO_2$, and of the true acid, $H.NO_3$, which is assumed to be present as hydroxonium nitrate, $(H.OH_2)(NO_3)$. The absorption spectrum and the electrical conductivity of nitric acid led to the inference that yet a third kind of molecule is present. Soln. of nitric acid in absolute sulphuric acid contain a largely ionized electrolyte which is more transparent than an equally conc. ethereal or aq. soln. of nitrate acid. Since soln. of acetic acid in absolute sulphuric acid, producing an acetylium cation, behave similarly, it is inferred that a **nitronium** cation is formed by dissolving nitric acid in absolute sulphuric acid, and the soln. contains **nitronium pyrosulphate,** $\{NO(OH)_2\}(HSO_4)$, and $\{N(OH)_2\}(HSO_4)_2$—*vide infra.* This hypothesis is confirmed by the isolation from soln. of perchloric acid in anhydrous nitric acid of **nitronium perchlorate,** $\{N(OH)_3\}(ClO_4)$, or of **nitronium oxyperchlorate,** $\{NO(OH)_2\}ClO_4$, by crystallization from perchloric acid and nitric acid respectively. R. Weber also isolated nitronium pyrosulphate, $\{NO(OH)_2\}HS_2O_7$, or $\{N(OH)_3\}S_2O_7$, in 1871—*vide infra.* The so-called nitrating acid—a mixture of conc. sulphuric and nitric acid—is assumed to contain **nitronium hydrosulphate,** $\{N(OH)_3\}(HSO_4)_2$, and not nitrogen pentoxide as suggested by A. Saposchnikoff. It is inferred that homogeneous nitric acid contains nitronium nitrate, $\{N(OH)_3\}(NO_3)_2$; and anhydrous nitric acid is considered to be a soln. of conducting nitronium nitrate in non-conducting pseudo-nitric acid—98·6 per cent. acid at 0° has 80 per cent. of pseudo-acid and 20 per cent. nitronium nitrate. The absorption spectra of aq. soln. show that nitronium nitrate is completely hydrolyzed by the addition of one mol. proportion of water, since from this point the absorption curves can be additively constructed from those of the pseudo-acid in ether and the true-acid in water. The conversion of the pseudo-acid into the true-acid (or its hydroxonium salt) is practically complete after the addition of 8 mols of water, whereas the dissociation at this point does not amount to 40 per cent. The last traces of the pseudo-acid have disappeared after addition of 50 mols of water, and the soln. then contains only hydroxonium salt which is not completely ionized, in the sense of the ionization theory, in 0·01*N*-soln. In the most dil. soln., the sole absorbent material is the nitrate ion; orthonitric acid and nitrogen pentahydrate do not exist (the so-called diacetylorthonitric acid, $N(OH)_3(OAc)_2$, is a molecular compound of the pseudo-acid, $[(CH_3.CO_2H)_2HO.NO_2]$).

The reactions between the three strongest oxyacids, perchloric, sulphuric, and nitric, give particularly strong evidence in favour of the chemical theory of acids according to which the strength (acidity) can be measured only chemically by their tendency towards salt formation, and not physically by their ability to furnish hydrogen-ions. According to the ionization theory, perchloric acid is the strongest acid, followed by nitric and then by sulphuric acids. Actually, homogeneous perchloric is incomparably stronger than nitric acid; and sulphuric acid, which is feebly ionized in aq. soln., is in the homogeneous condition stronger than nitric acid, since it causes the production of nitronium sulphate. In aq. soln., the great differences towards salt formation of the three acids are almost annihilated, since water as a basic anhydride. particularly in excess, and hence in dil. soln., converts them almost completely into hydroxonium salts.

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§ 44. The Physical Properties of Nitric Acid

The most conc. acid at ordinary temp. can be obtained as a colourless, transparent liquid. J. L. Proust[1] gave 1·62 for the highest **specific gravity** attainable, but this is a much greater value than others have been able to obtain—*e.g.* E. Mitscherlich, and R. Kirwan gave 1·54 at 20°; N. A. E. Millon, 1·55 at 15°; J. Pelouze, 1·52 at 15°; J. Kolb, 1·559 at 0°; and L. J. Thénard, 1·513. V. H. Veley and J. J. Manley found the sp. gr. of the most conc. acid to be 1·54212 at 4°; 1·52234 at 14·2°; and 1·50394 at 24·2°. F. Kohlrausch found the sp. gr. of the normal acid to be 1·0318 at 18°, and E. H. Loomis, 1·0324. Observations have been reported by E. Ruppin, R. Rehyer, G. B. Squire, C. Schultz-Sellack, T. Graham, D. I. Mendeléeff, O. Grotrian, H. Hager, G. W. Muncke, P. T. Meissner, H. Jahn and E. Schüler, W. H. Perkin, W. C. Röntgen and J. Schneider, A. V. Saposchnikoff, N. Tschernay, R. Wegner, and V. S. M. van der Willigen. Collections of data on the sp. gr. of aq. soln. of nitric acid of different concentrations have been made by C. F. Richter, A. Ure, H. Pützer, H. Goebel, F. Winteler, J. Kolb, etc. The results of G. Lunge and H. Rey are indicated in Tables XXXII and XXXIII. They refer to the contents of pure HNO_3; if nitrous acid or nitrogen peroxide be present, there will be less HNO_3 at the same sp. gr.—*vide* Table XXX. The correction for temp. is such that the amount indicated is to be added for every degree below 15°, and sub-

Table XXXII.—Specific Gravity and Composition by Weight of Nitric Acid.

(Sp. gr. at 15°/4° from 1·00 to 1·49, and from 1·500 to 1·520.)

	100 parts by weight contain HNO_3.									
	0	1	2	3	4	5	6	7	8	9
1·0	0·10	1·90	3·70	5·50	7·26	8·99	10·68	12·33	13·95	15·5
1·1	17·11	18·67	20·23	21·77	23·31	24·84	26·36	27·88	29·38	30·88
1·2	32·36	33·82	35·28	36·78	38·29	39·82	41·34	42·87	44·41	45·95
1·3	47·49	49·07	50·71	52·37	54·07	55·79	57·57	59·39	61·27	63·23
1·4	65·30	67·50	69·80	72·17	74·68	77·28	79·96	82·90	86·05	89·60
1·50	94·09	94·60	95·08	95·55	96·00	96·39	96·76	97·13	97·50	97·84
1·51	98·10	98·32	98·53	98·73	98·90	99·07	99·21	99·34	99·46	99·57
1·52	99·67	—	—	—	—	—	—	—	—	—

Table XXXIII.—Specific Gravity and Composition by Volume of Nitric Acid.

(Sp. gr. at 15°/4° from 1·00 to 1·49, and from 1·500 to 1·520.)

	One litre contains in kilograms of HNO_3.									
	0	1	2	3	4	5	6	7	8	9
1·0	0·001	0·019	0·038	0·057	0·075	0·094	0·113	0·132	0·151	0·169
1·1	0·188	0·207	0·227	0·246	0·266	0·286	0·306	0·326	0·347	0·367
1·2	0·388	0·409	0·430	0·452	0·475	0·498	0·521	0·544	0·568	0·593
1·3	0·617	0·643	0·669	0·697	0·725	0·753	0·783	0·814	0·846	0·879
1·4	0·914	0·952	0·991	1·032	1·075	1·121	1·168	1·219	1·274	1·335
1·50	1·411	1·420	1·428	1·436	1·444	1·451	1·457	1·464	1·470	1·476
1·51	1·481	1·486	1·490	1·494	1·497	1·501	1·504	1·507	1·510	1·512
1·52	1·515	—	—	—	—	—	—	—	—	—

Specific Gravity Corrections.

Sp. gr. .	1·000–1·020	1·020–1·040	1·040–1·070	1·070–1·100	1·100–1·130	1·130–1·160
± .	0·0001	0·0002	0·0003	0·0004	0·0005	0·0006
Sp. gr. .	1·160–1·200	1·200–1·245	1·245–1·280	1·280–1·310	1·310–1·350	1·350–1·365
± .	0·0007	0·0008	0·0009	0·0010	0·0011	0·0012
Sp. gr. .	1·365–1·400	1·400–1·435	1·435–1·490	1·490–1·500	1·500–1·520	—
± .	0·0013	0·0014	0·0015	0·0016	0·0017	—

tracted for every degree above that temp. This correction is applicable only when the temp. are near 15°. The results were confirmed by V. H. Veley and J. J. Manley, and W. R. Bousfield, and afford further evidence of the existence of hydrates in soln. Irregularities with 96–100 per cent. HNO_3 are connected with anhydrous formation. H. C. Jones measured the sp. gr. of dil. soln. and found:

	0·025*N*-	0·05*N*-	0·10*N*-	0·25*N*-	0·50*N*-	*N*-	2*N*-
Sp. gr. .	1·00093	1·00180	1·00350	1·00848	1·01686	1·03360	1·0670

From this and the lowering of the f.p. he inferred that the formation of hydrates does not begin until the soln. is over 0·75*N*. When nitric acid and water are mixed, there is a **contraction**, and J. Kolb found the maximum contraction occurs with a mixture corresponding with $2HNO_3.3H_2O$. On the other hand, F. W. Küster and R. Kremann found that although the vol. changes continuously, there are two deviations. Thus, expressing the vol. change, δv, in thousandths of the vol. at 0°, they found between —15° and 0°:

HNO_3	25	45	50	54	60	70	77·7	80	89·4 per cent.
δv .	6·8	10·6	11·9	11·9	13·2	14·6	13·2	14·2	14·9

The one break occurs with about 54 per cent. HNO_3, and corresponds with $HNO_3.3H_2O$; while the other break occurs with about 77·77 per cent. HNO_3, and corresponds with $HNO_3.H_2O$. These deviations probably represent the formation of the mono- and tri-hydrates. J. N. Rakshit studied this subject. P. Wright found that the temp. of **maximum density** of water is lowered 0·8° in $\frac{1}{16}N$-HNO_3 ; 1·6° in $\frac{1}{8}N$-soln. ; and 3·1° in $\frac{1}{4}N$-soln. V. H. Veley and J. J. Manley found that for acids containing 78 to 99·97 per cent. of HNO_3, the contraction $\times 10^5$ is $4660-205\delta\omega$ at 4° ; $4590-208\delta\omega$ at 14·2° ; and $4623-19\delta\omega$ at 24·2°, where $\delta\omega$ represents the percentage difference of HNO_3. M. Berthelot expressed the **molecular volume** of soln. of nitric acid containing N- mols of water per mol of HNO_3, by mol. vol. $=18N+29+39(N+3{\cdot}2)^{-1}$. W. Grunert found that the sp. gr. of mixtures of nitric acid and potassium nitrate at 20 increased proportionally with the concentration over the whole range examined. S. Sugden discussed the mol. vol. of nitric acid.

The effect of temp. on the sp. gr., or the **thermal expansion** of dil. aq. soln. of nitric acid, has been measured by C. Forch, and W. Ostwald ; and of conc. soln., by F. W. Küster and R. Kremann, who found breaks in the otherwise continuous curve corresponding with $HNO_3.3H_2O$ when 54·00 per cent. HNO_3 is present, and with $HNO_3.H_2O$, when 77·77 per cent. nitric acid is present. V. H. Veley and J. J. Manley measured the coeff. of cubical expansion, α, of nitric acid and found :

	4° to 14·2°				14·2° to 24·2°			
HNO_3	25·5	51·2	75·6	100·0	25·5	51·2	75·6	100·0 per cent.
α .	0·000550	0·000942	0·000088	0·001274	0·000585	0·000907	0·001076	0·001240

G. Forch's results for $\delta v=(v-1)$ are

	5°	10°	15°	20°	30°	40°
0·5N-HNO_3 . .	0·00039	0·00108	0·00203	0·00323	0·00628	0·01011
0·999N-HNO_3 . .	0·00084	0·00190	0·00317	0·00466	0·00817	0·01239
1·998N-HNO_3 . .	0·00153	0·00321	0·00503	0·00699	0·01131	0·01612

Observations were also made by V. H. Veley and J. J. Manley, while W. R. Bousfield found for the sp. gr. of soln. with $\frac{1}{32}N$-HNO_3 to N-HNO_3 :

	N-	$\frac{1}{2}N$-	$\frac{1}{4}N$-	$\frac{1}{8}N$-	$\frac{1}{16}N$-	$\frac{1}{32}N$-
4° . .	1·035801	1·018011	1·009031	1·004533	1·002271	1·001130
11° . .	1·034339	1·017082	1·008386	1·004040	1·001852	1·000748
18° . .	1·032439	1·015616	1·007160	1·002931	1·000802	1·999731
25° . .	1·030163	1·014707	1·005445	1·001309	1·999235	0·998192

The sp. gr. of mixtures of sulphuric and nitric acids was measured by E. Roberts, and P. Pascal and M. Garnier—for some of A. V. Saposchnikoff's results, *vide infra*, electrical conductivity. According to A. Marshall the following represents the sp. gr. of the mixtures at 18°/18° when the sp. gr. of the sulphuric acid is 1·8437, and of nitric acid, 1·5009 :

	0·52	4·67	9·10	22·51	39·49	57·78	72·89	98·19
Sp. gr. .	1·8456	1·8586	1·8605	1·8215	1·7601	1·6879	1·6227	1·5080

D. Colladon and C. Sturm[2] found the coeff. of **compressibility** of nitric acid at 0° between 1 and 32 atm. press. to be 0·000032 ; and W. C. Röntgen and J. Schneider obtained respectively 0·958 and 0·981 for the relative compressibility (water unity) of soln. of nitric acid respectively containing 1500 and 700 mols. of HNO_3 per gram of water. S. Pagliani and E. Oddone found the **viscosity** coeff., η, of nitric acid to be :

HNO_3 .	100	72·85	67·82	64·30	61·56	58·10	53·90 per cent.
η at 0° .	0·02275	0·03276	0·03422	0·03560	0·03459	0·03295	0·02945
η at 10° .	0·01770	0·02456	0·02579	0·02676	0·02604	0·02470	0·02324

If that of water be unity, R. Reyher found the viscosity of N-HNO_3 to be 1·0266 at 25° ; $\frac{1}{2}N$-HNO_3, 1·0115 ; $\frac{1}{4}N$-HNO_3, 1·0052 ; and $\frac{7}{8}N$-HNO_3, 1·0027. T. Graham made some observations on this subject; and F. W. Küster and R. Kremann found water unity at 0°:

HNO_3	98·5	82·0	70·0	65·0	50·0	30·0	10·0
η at 15°	0·548	1·036	1·277	1·300	1·144	0·822	0·655
η at −15°	0·833	2·240	3·268	3·304	2·369	2·635	—

W. R. Bousfield gave for the viscosity coeff. between 4° and 25°:

	4°	11°	18°	25°
N-	0·015487	0·012807	0·010731	0·009176
$\frac{1}{2}N$-	0·015513	0·012684	0·010590	0·009011
$\frac{1}{4}N$-	0·015552	0·012655	0·010546	0·008696
$\frac{1}{8}N$-	0·015586	0·012651	0·010519	0·008943
$\frac{1}{16}N$-	0·015605	0·012663	0·010525	0·008927
$\frac{1}{32}N$-	0·015630	0·012672	0·010528	0·008920
Water	0·015666	0·012672	0·010514	0·008901

These results calculated for water are plotted in Fig. 91. The explanation of the maxima in the curves depends on the complex structure of the water molecule (1. 9, 7). L. J. Simon also studied the viscosity of nitric acid. W. Grunert found that the viscosities of mixtures of nitric acid and potassium nitrate at 20°, increase over the whole range of concentration examined. E. C. Bingham and S. B. Stone measured the fluidity of mixtures of soln. of nitric and sulphuric acids at 10°, 20°, and 40°.

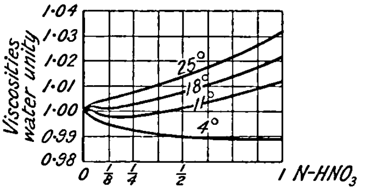

FIG. 91.—Viscosity of Nitric Acid of Various Concentrations at Different Temperatures.

O. Jahnke found the **surface tension,** σ dynes per cm., and the **specific cohesion,** a^2 sq. mm., of nitric acid with p per cent. of HNO_3, at 20°, to be:

p	7·25	9·00	22·00	37·00	50·00	70·00
σ	73·10	72·70	71·48	68·10	65·43	59·36
a^2	14·34	14·07	12·82	11·23	10·13	8·66

E. Aston and W. Ramsay found for nitric acid of sp. gr. 1·5304, σ=41·30 at 11·6°; sp. gr. 1·4696, σ=35·95 at 46·2°; and of sp. gr. 3·806, σ=31·46 at 78·2° (by extrapolation). This gives the molar **surface energy** $\sigma(Mv)^{\frac{2}{3}}$, 492·3, 440·4, and 395·6 ergs, and the results show that liquid nitric acid probably consists of a mixture of mols of HNO_3 and $(HNO_3)_2$. The evidence favours the view that negative curvature is due to some form of dissociation, whilst positive curvature is brought about by solvation. The conc. of the mixture showing the maximum deviation from the linear fluidity-vol. conc. curve is independent of the temp., provided that only one solvate is formed, and in such favourable cases it is believed that this conc. may be utilized for finding the composition of the solvate.

The velocity of **diffusion** of nitric acid in water was studied by S. Arrhenius, J. H. Long, J. J. Coleman, G. Umoff, and J. Stefan. The results of J. D. R. Scheffer at 9°, and of J. Trovert at 19·5°, for the coeff. of diffusion, k, in sq. cm. per day, and with the conc., C mols per litre, are as follow:

C	0·04	0·44	3·56	0·02	0·90	3·90
k	1·73	1·78	1·94	2·12	2·26	2·46

while L. W. Oholm gave for 20°, $2N$-, k=2·150; $1·5N$-, k=2·141; N-, k=2·164; $0·5N$-, k=2·227; $0·1N$-, k=2·246; and for $0·05N$-, k=2·266. Y. Terada measured the speed of dialysis.

About 1777, C. W. Scheele[3] found that when the vapour of nitric acid is passed through a white-hot tube, it decomposes into nitrogen and oxygen; but if the tube is not heated to a very high temp., only oxygen and nitrogen peroxide are formed. P. Braham and J. W. Gatehouse, and H. Böttger said that when nitric acid is heated all the nitrogen oxides as well as nitrogen and oxygen are produced. L. Carius found that nitric acid is entirely decomposed at 256° in accord with the equation $4HNO_3=4NO_2+2H_2O+O_2$; and measuring the progress of the decomposition by the vap. density, D, at different temp. (air unity), he found:

	86°	100°	130°	160°	190°	220°	250°	256°	265°	312°	
D .	2·05	2·02	1·92	1·79	1·59	1·42	1·29	1·25	1·24	1·23	
a .	9·53	11·77	18·78	28·96	49·34	72·07	93·03	100·00	—	—	per cent.
v .	9·43	10·41	16·62	26·22	43·69	63·77	82·30	88·47	—	—	c.c.

The penultimate line represents the calculated percentage decomposition, a; and the last line, the vol. of oxygen, v c.c., obtained per gram of nitric acid. M. Berthelot showed that nitric acid sealed in evacuated tubes and kept in the dark remains unaltered for several weeks at ordinary temp., but at 100°, the nitric acid decomposes into nitrogen peroxide, oxygen, and water. The decomposition is incomplete, and is limited by the water produced, for, under similar conditions, nitric acid of sp. gr. 1·333 suffers no change at 100°. The decomposition can scarcely be regarded as reversible, since the oxygen will combine very slowly with any nitrous acid that may be formed by the action of the nitric peroxide on the water. The decomposition of nitric acid into nitric peroxide, oxygen, and water at 100° would absorb about —6·5 Cals. per mol. of acid. The decomposition of nitric anhydride absorbs much less, hence the instability of this compound. On the other hand, the heat of formation of hydrated nitric acid is much higher than that of the anhydrous acid, hence the greater the stability of the former.

J. C. G. de Marignac [4] found the **specific heat** of soln. with 58·3, 12·3, and 3·4 per cent. HNO_3 to be respectively 0·6651, 0·8752, and 0·9618 between 21° and 52°; and J. Thomsen, for soln. with 26, 15, and 3·4 per cent. HNO_3, respectively 0·768, 0·849, and 0·963 at 18°. T. Thomson, and T. W. Richards and A. W. Rowe also measured the sp. ht. of nitric acid. N. de Kolossowsky discussed the sp. ht. of soln. of the acid. P. Pascal and M. Garnier obtained results for nitric acid, and for mixtures with nitrogen peroxide and with sulphuric acid. They gave for the mean sp. ht. of nitric acid at 20°:

HNO_3 .	10·00	25·27	40·00	45·87	60·52	70·00	81·80	90·33	92·15	98·15	per cent.
N_2O_4 .	—	—	—	—	—	0·70	1·54	2·30	4·22	1·85	„
Sp. ht. .	0·900	0·787	0·669	0·662	0·637	0·610	0·575	0·530	0·500	0·475	

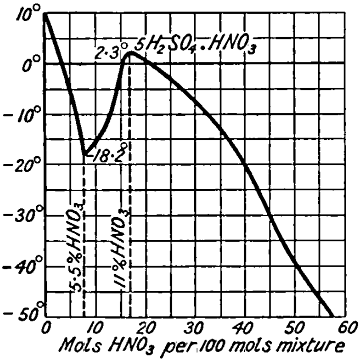

FIG. 92.—Freezing-point Curve of Binary Mixtures: HNO_3–H_2SO_4.

J. Dalton gave —19° for the **melting point** of nitric acid of sp. gr. 1·30; and F. W. Küster and S. Münch for absolute nitric acid —41°. A. Hantzsch and L. Wolf gave —42·3° for the m.p. of absolute nitric acid. This subject has been already discussed in connection with the hydrates of nitric acid, Fig. 92. E. H. Loomis,[5] H. C. Jones, and H. C. Jones and F. H. Getman measured the **lowering of the freezing point** of water by nitric acid, and found that when a litre of soln. contains n mols of HNO_3, the lowering of the f.p., $\delta\theta$, and the calculated percentage ionization, a, for dil. soln. are as follow:

n .	0·001054	0·003158	0·007378	0·1153	0·05103	0·1059
$\delta\theta$.	0·0040°	0·0119°	0·0276°	0·4300°	0·1892°	0·3735°
a .	100	99·4	97·9	97·3	95·8	86·6 per cent.

W. C. Holmes measured the f.p. of mixtures of sulphuric acid with up to 50 per cent. of nitric acid. If no water be present so that the total acidity is 100 per cent. there is a minimum at —18·2° when 5·4 per cent. HNO_3 is present; and a maximum at 2·3° with 10·8 per cent. HNO_3. This corresponds with **nitratopentasulphuric**

acid, $HNO_3.5H_2SO_4$. If the total acidity be 95 per cent., the f.p. falls to —41° with 2·35 per cent. HNO_3; rises to a maximum at —11° with 9·75 per cent. HNO_3; and falls to —41·3° with 49·09 per cent. HNO_3; when the total acidity is 103 per cent., there is a minimum at —12·3° with 8·15 per cent. HNO_3, and a maximum at 10·5° with 15·52 per cent. HNO_3. In both cases, the results are complicated by water and sulphur trioxide respectively.

A. V. Saposchnikoff [6] measured the **vapour pressure** of soln. of nitric acid, at 15°, and his results are as follow:

Sp. gr. . .	1·400	1·453	1·462	1·487	1·497	1·510
HNO_3 . .	65·30	78·10	82·10	88·65	92·93	98·00 per cent.
Pressure .	1·90	9·40	16·64	29·70	42·60	46·20 mm.
N_2 in vapour .	19·32	22·52	22·65	23·05	23·50	23·75 per cent.

Since nitric acid contains 22·22 per cent. of nitrogen, some nitrogen oxides must also be present in the vapour from the conc. acid; and water vapour, from the dil. acid. H. J. M. Creighton and J. H. Githens gave for the vap. press., p mm., at different temp:

HNO_3 .	0	20	30	40	50	60	70	80	90	100 per cent.
p at 75° .	289	260	230	195	155	135	115	170	295	524
p at 85° .	434	290	350	300	250	225	195	250	440	725
p at 95° .	634	554	497	435	375	330	300	375	625	—
p at 100° .	760	663	585	510	450	405	370	450	745	—

The curves thus show a minimum vap. press., Fig. 93, and there is also a corresponding maximum in the b.p. curves. A. Klemenc and A. Nagel found for the partial press., p mm., of water and HNO_3 over aq. soln. of nitric acid at 12·5°, and 30°:

	HNO_3	0	N-	$2N$-	$5N$-	$10N$-	$15N$-	$20N$-	$24N$-
12·5°	p_{HNO}	—	—	0·030	0·0181	0·526	1·19	10·80	25·69
	p_{H_2O}	10·87	10·44	9·99	8·19	4·88	1·22	—	—
30°	p_{HNO_3}	—	—	0·0070	0·0482	0·641	3·28	—	—
	p_{H_2O}	31·77	30·72	29·42	24·07	13·88	2·95	—	—

C. L. Burdick and E. S. Freed also made analogous observations for acid with 24·1 to 69·9 per cent. HNO_3 at 25°, 50°, and 75°. G. B. Taylor tabulated the available data. The vap. press. of mixtures of nitric and sulphuric acids rises and falls with increasing proportions of nitric acid. P. Pascal studied the variations in the conc. of the nitric acid in the vapours emitted on distillation. A. V. Saposchnikoff's results are shown in Fig. 94. The maximum for nitric acid of sp. gr. 1·40 occurs at 23·5 mm. with 45 per cent. HNO_3; for nitric acid of sp. gr. 1·48, at 34 mm. with

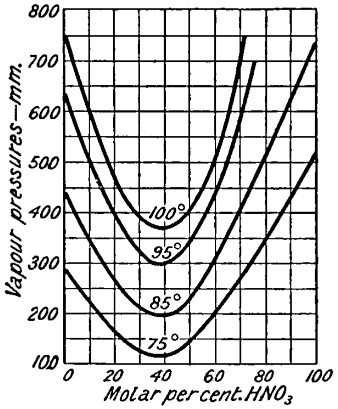

FIG. 93.—Vapour Pressure Curves of Nitric Acid.

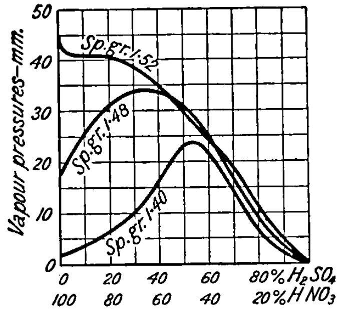

FIG. 94.—Vapour Pressures of Mixtures of Nitric and Sulphuric Acids.

67 per cent. HNO_3; and with an acid of sp. gr. 1·52, the value falls to from 46 mm. to 41 mm. with about 92 per cent. HNO_3 and remains constant to about 80 per cent. HNO_3, when it falls steadily as indicated in the diagram, Fig. 94. E. Oeman found the constant boiling acid contains 68 per cent. HNO_3; and the distillation curve shows that at conc. over 92 per cent. HNO_3, dissociation does not occur in accord with the electrical conductivity measurements. W. C. Sproesser and G. B. Taylor measured the vap. press. of 20–80 per cent. acids between 0° and 80°. With acid above 90 per cent. HNO_3, decomposition occurred at all temp. above 0°.

H. E. Roscoe said that the **boiling point** of the most conc. acid is 86° at 760 mm. press., but decomposition occurs before this temp. is attained; and H. Erdmann gave 21·5° at 24 mm. press. The influence of press. on the b.p. given by H. J. M. Creighton and J. H. Githens for an acid with 99·7 per cent. HNO_3 is as follows:

Press.	47	60	110	203	290	360	500	675 mm.
B.p.	22·1°	26·2°	35·6°	49·0°	57·1°	63·4°	72·7°	82·5°

Their results for the boiling points of aq. soln. of nitric acid of different conc. and at different press. are given in Table XXXIV. J. Dalton pointed out that when conc. or dil. soln. of nitric acid are boiled at atm. press., the b.p. gradually rises to 120·5°, and the composition of the distillate then does not change. The fact was subsequently confirmed by E. Mitscherlich, N. A. E. Millon, A. Smith, A. Bineau, and H. W. F. Wackenroder. The soln. of constant b.p. was found by H. E. Roscoe to contain 68 per cent. of HNO_3, and to have a sp. gr. of 1·414 at 15·5°. If this soln. be distilled under an increased or decreased press., the composition of the constant boiling soln. has a different concentration for each change of press. In illustration, H. J. M. Creighton and J. H. Githens found the maximum b.p. is 121·70° and 760 mm. when 68·18 per cent. HNO_3 is present; 99·9° at 360 mm. when 67·15 per cent. HNO_3 is present; and 74·2° at 110 mm. when 66·8 per cent. HNO_3 is present. Hence, argued H. E. Roscoe, the soln. with 60 per cent. of HNO_3 does not contain a definite hydrate; if it did, the composition would remain constant through a definite range of press. and temp. The b.p. curves of nitric acid for 760 mm. and 360 mm. are shown in Fig. 97. C. D. Carpenter and J. Babor distilled dil. nitric acid without a fractionating column, and found that with successive portions

Table XXXIV.—Boiling Points of Nitric Acid of Different Concentrations and at Different Pressures.

Per cent. HNO_3	Molecular per cent. HNO_3	Boiling point.				Vapour pressure mm.			
		760 mm.	360 mm.	250 mm.	110 mm.	75°	85°	95°	100°
0	0	—	—	—	—	289	434	634	760
20	6·7	103·56	84·7	74·5	56·4	260	390	534	663
30	11·0	108·08	87·2	76·6	59·3	230	350	497	585
40	16·8	112·58	91·1	80·0	63·6	195	300	435	510
50	22·0	116·84	95·4	84·1	68·3	155	250	375	450
60	30·2	120·06	98·7	87·5	71·6	135	225	330	405
70	40·1	121·60	99·9	89·7	73·7	115	195	300	370
80	53·5	115·45	94·0	83·1	66·8	170	250	375	450
90	72·6	102·03	79·5	69·5	50·2	295	440	625	745
100	100·0	—	—	—	—	524	725	—	—

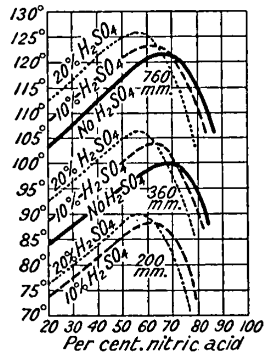

Fig. 95.—Boiling Points of Solutions of Nitric Acid with and without Sulphuric Acid.

of the distillate there was a loss of 3 per cent. of the nitric acid in concentrating from 10 per cent. to 20 per cent. HNO_3, 9·3 per cent. between 20 and 30 per cent. HNO_3, and 20·9 per cent. between 30 and 40 per cent. HNO_3. The curve representing the relation between the vol. of the residual soln. and the conc. of nitric acid contained therein is a regular hyperbola, terminating at a point corresponding to the constant b.p. mixture. Concentration under the conditions described is therefore not economically possible.

The effect of sulphuric acid on the b.p. was measured by H. J. M. Creighton and H. G. Smith, and the results are indicated in Fig. 95. P. Pascal represented the b.p. of the ternary system: HNO_3–H_2SO_4–H_2O, as a surface over the triangular diagram; this subject was also examined by M. Kaltenbach. H. J. M. Creighton and H. G. Smith showed that the presence of potassium hydrosulphate in the nitric acid raises the b.p. of the mixture, but this is not attended by any appreciable change in the composition of the mixture of maximum b.p., but additions of sulphuric acid to aq. nitric acid cause a decrease in the HNO_3 content of the mixture of maximum b.p., and this the more the greater the amount of H_2SO_4 present. Thus, at 760 mm. press. the maximum b.p. occurs at 68·18 per cent. HNO_3 with no sulphuric acid; with 64·5 per cent. HNO_3 and 10 per cent. H_2SO_4; and with 59·2 per cent. HNO_3 and 20 per cent. H_2SO_4. Hence, with 68 per cent. aq. soln. of nitric and 20 per cent. sulphuric acids, a conc. acid distils over until acid of maximum b.p. is obtained. This shows why 68–69 per cent. HNO_3 soln. of nitric acid can be conc. to over 90 per cent. HNO_3 by distillation with conc. sulphuric acid; potassium hydrosulphate is of little use in this direction. The effect of reducing the press. is to make the mixture of maximum b.p. still less conc., and thus favour the concentration of the more conc. acid. The distillation of these mixtures was further studied by P. Pascal and M. Garnier, E. Galle, J. Baumann, L. Ramberg, and E. Berl and O. Samtleben. E. Oeman said that no dissociation occurs in the distillation of acid of conc. over 92 per cent.

The **heat of formation** given by J. Thomsen[7] is (H,N,3O)=41·51 Cals.; (H,NO,2O) =63·085 Cals.; (NO_2,O,H)=43·515 Cals.; and $\frac{1}{2}(N_2O_4,O,H_2O)$=18·67 Cals. M. Berthelot gave (H,N,3O)=34·0 Cals. for the gas, 41·6 Cals. for the liquid, 42·2 Cals. for the solid, and 48·8 Cals. for the soln. M. Berthelot gave 7·18 Cals. for the **heat of solution,** and J. Thomsen, 7·49 Cals. The former also gave the following data marked B, and J. Thomsen those marked T, for the heat of dilution of a mol of HNO_3, with *n* mols of water, at 10°:

n	0·5	1·0	1·5	2·0	3·0	4·0	5·0
Cals. B	2·03	3·34	4·16	4·86	5·76	6·39	6·76
Cals. T	2·005	3·285	4·16	—	5·71	—	6·665
n	6	8	10	20	40	100	200
Cals. *B*	6·98	7·22	7·27	7·36	7·27	7·21	7·18
Cals. *T*	—	—	7·318	7·458	7·436	7·439	7·493 (320)

He also found 7580 cals. for the heat of soln. of a mol of HNO_3 in 320 mols of water; for $HNO_3.H_2O$, 4280 cals.; for $HNO_3.2H_2O$, 2740 cals.; and for $HNO_3.3H_2O$, 1830 cals. Observations were also made by G. Rousseau and G. Tite, S. U. Pickering, T. W. Richards and A. W. Rowe, and J. Petersen. M. Berthelot gave for the **heat of fusion** of HNO_3, 9·54 Cals. per gram, or 601 Cals. per mol; and for the **heat of vaporization,** 115·1 Cals. per gram, or 7250 Cals. per mol. For the **heat of neutralization** of HNO_3 with an eq. of sodium hydroxide, M. Berthelot gave 13·68 Cals.; potassium hydroxide, 13·77 Cals.; ammonium hydroxide, 12·32–12·6 Cals.; thallium hydroxide, 13·69 Cals.; calcium hydroxide, 13·9 Cals.; strontium hydroxide, 13·9 Cals.; barium hydroxide, 13·9–14·13 Cals.; magnesium hydroxide, 13·76 Cals.; zinc hydroxide, 9·8–9·915 Cals.; cadmium hydroxide, 10·16 Cals.; manganese hydroxide, 11·475 Cals.; ferrous hydroxide, 10·475 Cals.; cobaltous hydroxide, 10·55 Cals.; nickelous hydroxide, 10·55 Cals.; cupric hydroxide, 7·445 Cals.; cupric oxide, 7·625 Cals.; silver oxide, 5·2–5·44 Cals.; mercuric oxide, 3·105–3·65 Cals. (R. Varet); mercurous oxide, 2·895–9·1 Cals. (R. Varet); lead oxide, 8·385–8·885 Cals.; and uranyl hydroxide, H_2UO_4, 4·2 Cals. (J. Aloy). P. Dutoit and E. Grobet measured the rise of temp. during the progressive neutralization of various bases with nitric acid with the idea of detecting the formation of basic salts, etc. J. H. Mathews and A. F. O. German gave for $2N$-, $1N$-, $\frac{1}{2}N$- and $\frac{1}{4}N$-NaOH, respectively 13·636, 13·614, 13·647, and 13·548 Cals.; and A. Wörmann

	6°			18°			32°		
	$\frac{1}{4}N$-	$\frac{3}{16}N$-	$\frac{1}{8}N$-	$\frac{1}{4}N$-	$\frac{1}{8}N$-	$\frac{1}{20}N$-	$\frac{1}{4}N$-	$\frac{1}{8}N$-	$\frac{1}{20}N$-HNO_3
KOH	14·472	14·402	14·405	13·912	13·838	13·864	13·103	—	13·087 Cals.
NaOH	14·399	14·345	14·324	13·708	13·686	13·695	12·928	12·892	12·935 Cals.

Observations on this subject were also made by T. W. Richards and A. W. Rowe, T. Andrews, and J. Thomsen. D. D. Karve studied the heats of soln. in alcohol, and ether. The heat developed by oxidizing reactions with nitric acid was discussed by M. Berthelot in 1880. J. W. McDavid studied the heat developed on mixing soln. of nitric and sulphuric acids, and his results, expressed in gram-calories per gram of product—when the mixed acid is produced from 100 per cent. nitric acid, 100 per cent. sulphuric acid, and water—are shown in Fig. 96. C. L. Burdick and E. S. Freed calculated the free energy of nitric acid vapour at 10°, 50°, and 75° to be respectively, −16,750 cals., −16,240 cals., and −14,720 cals.; or, at $T°$ K., $-25510+31T$; and for soln. of nitric acid:

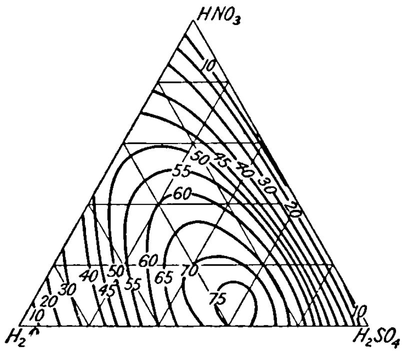

FIG. 96.—Heat developed on Mixing Nitric and Sulphuric Acids and Water.

HNO_3		5	10	20	30	40	50	60	70 per cent. wt.
Free Energy	25°	−24250	−23560	−22820	−22190	−21570	−20900	−20190	−19350
	50°	−23040	−22270	−21410	−20640	−20040	−19370	−18700	−18000
	75°	−21700	−20770	−19820	−19070	−18440	−17780	−17110	−16500

The **index of refraction** μ, of nitric acid was measured by J. H. Gladstone,[8] and J. H. Gladstone and W. Hibbert found that the value is changed only a little by dilution. J. W. Brühl found for the D-line with nitric acid of sp. gr. 1·50999 at 20°/4°, $\mu=1·39584$, and with an acid of sp. gr. 1·50875, $\mu=1·36870$; the corresponding mol. **dispersion** was 0·338 and 0·340. V. H. Veley and J. J. Manley found for sodium light at 14·2°:

HNO_3	2·19	11·88	70·04	71·57	89·88	95·66	98·67	99·87 per cent.
μ	1·336208	1·349371	1·406094	1·406046	1·401419	1·398148	1·396908	1·397167

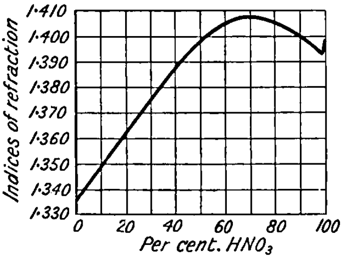

FIG. 97.—Refractive Indices of Nitric Acid.

There is a slow increase as the conc. of the acid increases up to about 70 per cent. HNO_3 when a maximum is attained—Fig. 96; the values then decrease slowly to about 91 per cent. HNO_3, and thereafter more quickly to 98·67 per cent. HNO_3 when there is a slight increase. The value for the anhydrous acid is nearly the same as that for an acid with 50 per cent. HNO_3. J. H. Gladstone gave 17·24 for the **refraction equivalent** of nitric acid. J. A. Wasastjerna made observations on this subject. J. C. Ghosh and S. C. Bisvas measured the extinction coeff. in the ultra-violet. C. V. Raman found that the light scattered by dust-free nitric acid is nearly always unpolarized; and he said that W. L. Bragg's observations on the scattering of light by nitric acid support the hypothesis that the nitric acid molecule and the NO_3-ion are anisotropic. S. Venkateswaran, C. V. Raman, and C. W. Sweitzer studied the scattering of light by nitric acid. W. H. Perkin measured the **magnetic rotatory power** at 15°, and found the specific rotation, the molecular rotation, and the molecular rotation less that of water, to be :

HNO_3 . . .	99·45	56·44	32·36	26·81	22·54 per cent.
Specific rotation .	0·5292	0·8042	0·9066	0·9238	0·9350
Molecular rotation .	1·226	3·678	8·163	10·360	12·783
Mol. rot. less water .	1·207	0·977	0·852	0·805	0·753

C. Féry examined the effect of the progressive addition of sodium hydroxide to a soln. of nitric acid on the index of refraction, and found the maximum deviation corresponded with the ratio $NaOH : HNO_3$. R. Wachsmuth made some measurements of this constant. W. N. Hartley observed the **absorption spectra** of nitric acid and found that with 89·60 per cent. HNO_3, the spectrum is continuous to 2644 with a weak extension at 3685, and between 2718 and 2743 ; with 72·57 per cent. acid, the spectrum is continuous to 3079 with a weak extension between 3105 and 3150 ; and with acids between 69·80 and 2031 per cent. HNO_3, the spectrum is continuous to 3079. The acid of sp. gr. 1·432 in thickness 2 mm. transmits a longer spectrum than the same acid diluted to 36 times its vol. in thickness 100 mm. The marked changes in the spectra with acids of sp. gr. approximating 1·432 are 1·490, led to the assumption that there is some chemical action going on between the water and the acid, when the conc. change. K. Schaefer and co-workers found that soln. of the nitrates exhibit selective absorption, while the alkyl nitrates cut off only the ultra-violet end of the spectrum. Dil. nitric acid has a spectrum like that of the salts, but with a conc. above $2N$-HNO_3, the ester type appears, and with the conc. acid, there is only continuous absorption. The absorption spectrum of nitric acid vapours is very like that of 98·7 per cent. HNO_3. Hence, the NO_3-group in the vapour is very similar to that in the ester, and the conc. acid. The absorption limit of $0{\cdot}2N$-HNO_3 is displaced towards the ultra-violet by 20 per cent. of sulphuric acid, and at the same time, the absorption curve is flattened ; this effect increases with increasing conc. of sulphuric acid. Sulphuric acid displaces the equilibrium between the two types of the nitrate spectrum. Observations were also made by G. Massol and A. Faucon, W. J. Pope, R. A. Morton and R. W. Riding, and by E. Siegler-Soru. E. C. C. Baly and co-workers found that in alcoholic soln. the ester type of absorption occurs, and in aq. soln. increasing dilution brings out the nitrate bands more clearly, corresponding with W. N. Hartley's suggestion that the band is due to ionized nitrate. C. Schaefer and M. Schubert found that the ultra-red reflection spectra of a number of nitrates show λ^{-1} three maxima, at approximately $7{\cdot}5\mu$, $12{\cdot}5\mu$, and $15{\cdot}0\mu$; in addition, mercurous nitrate shows a fourth maximum at $10{\cdot}08\mu$ with ordinary light. The three maxima, observed with the biaxial nitrates, with ordinary light, are made up of three components corresponding respectively with the vibrations parallel to the axes of the three indices of refraction. The characteristic vibrations, as in the case of the carbonates and sulphates, depend very slightly on the metal, and are due to internal vibrations of the NO_3-group, which are practically the same in all the nitrates examined.

According to F. Kohlrausch and O. Grotrian,[9] the **electrical conductivity** of nitric acid increases as the conc. increases up to 30–33 per cent. HNO_3 and thereafter decreases. Measurements were also made by H. Crompton, E. Bouty, F. W. Küster and R. Kremann, R. Lenz, etc. According to V. H. Veley and J. J. Manley, the specific conductivity of nitric acid in $K \times 10^8$ mercury units at 15° is :

HNO_3 .	1·30	3·12	20·11	30·42	51·78	78·96	94·32	98·50	99·34 per cent.
$K \times 10^8$	632·06	1440·6	6363·8	7008·2	5554·2	1945·1	207·8	167·81	387·34

The more detailed results, plotted in Fig. 98, show that the conductivity rapidly increases with concentration up to a maximum at about 30 per cent. HNO_3, and then there is a decrease until a minimum is reached with 96·12 per cent. HNO_3. F. W. Küster and R. Kremann detected two irregularities in the conductivity curve of soln. containing 25 and 50 per cent. of HNO_3 corresponding respectively with the tri- and monohydrates; and a third irregularity with between 96–100 per cent. HNO_3, at which the concentration irregularities occur with sp. gr. and f.p. curves, and is concerned with the formation of the anhydride. A. Hantzsch and L. Wolf could detect no minimum in the conductivity of soln. of nitric acid. The minimum value for the conductivity of 99·5 per cent. HNO_3 is 89×10^{-4} at 0°, whereas an almost absolute acid gave 94×10^{-5} at $-40°$. Observations on dil. soln. were made by W. Ostwald, S. Arrhenius, E. H. Loomis, H. C. Jones and F. H. Getman, etc. According to F. Kohlrausch and O. Grotrian, the eq. conductivity, λ, for soln. with a mol of HNO_3 in v litres of water at 18° is:

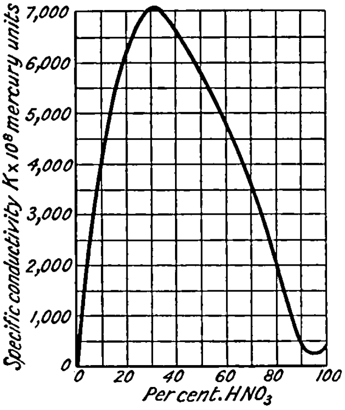

FIG. 98.—Specific Electrical Conductivity of Nitric Acid at 15°.

v	0·1	0·2	0·5	1	2	5	20	100	500	1000
λ	65·4	156	258	310	324	340	357	368	375	(375)

S. Arrhenius gave for the conductivity, λ, at $\theta°$, $\lambda = \lambda_0 e^{-0{\cdot}0014\theta}(1 + 0{\cdot}0157\theta)$; there is a maximum value for the conductivity at 167°, *i.e.* when $(1 + 0{\cdot}0157\theta)0{\cdot}0014 = 0{\cdot}0014$. Working with soln. containing M milliformula-weight per litre at 4°, A. A. Noyes found the effect of temp. on the conductivity of the soln. to be:

		18°	25°	50°	75°	100°	128°	156°	218°	306°
M	0·5	374·0	417·0	563·9	697·2	815·0	930·9	1029·0	—	—
	2·0	371·2	413·7	558·8	689·7	786·0	919·0	1012·0	1166	1158
	10·0	365·0	406·0	548·0	676·0	782·7	893·0	978·0	—	—
	12·5	363·9	405·0	546·2	673·4	750·1	887·0	972·0	—	—
	50·0	353·7	393·3	528·6	649·4	751·2	847·4	921·4	—	—
	80·0	349·0	388·0	521·0	637·0	735·0	827·0	873·0	926	454
	100·0	346·4	385·0	515·9	632·5	729·9	820·0	885·7	—	—

E. Bouty found that nitrates dissolved in conc. nitric acid raise the conductivity in proportion to the amount dissolved. A. Klemenc and R. Schöller measured the conductivity of mixtures of nitrous and nitric acids, but obtained no definite evidence of the existence of $H_2N_3O_8$. Observations on the temp. coeff. were made by F. Kohlrausch and O. Grotrian, C. Déguisne, and J. and G. E. Gibson. According to S. Arrhenius, the temp. coeff. between 18° and 52°, is:

v	2	10	100	1000	∞
Temp. coeff. . . .	0·0143	0·0147	0·0152	0·0154	0·0157

V. H. Veley and J. J. Manley said that nitric acid at conc. above 94 per cent. HNO_3 behaves like a metallic conductor in having a negative temp. coeff. H. C. Jones found for the mol. conductivity, μ, and percentage **degree of ionization,** α, for soln. with a mol of the salt in v litres at 0°.

v	0·5	1·0	2	4	10	20	40	60
μ	177·15	203·72	216·63	222·82	226·24	233·88	234·89	238·07
α	74·71	85·93	91·38	93·99	95·43	98·65	99·08	100·00

It is inferred that in dil. soln. there is no tendency to form hydrates; and from the f.p. data, it is concluded that hydration does not begin until the soln. is 0·75N-. For soln. with M mols of HNO_3 per litre, he calculated that H mols of water were in combination with a mol of the salt at the given conc. of a litre of the soln., at that conc., contained 1000 grms. of water.

M	0·6	0·8	1·0	12·0	3·0	4·0	5·0	6·0
H	2·07	3·41	3·76	5·06	5·18	6·02	5·83	5·09

H. Crompton found that the second differential coeff. of the electrical conductivity and the composition of soln. agree with the presence of the hydrates $HNO_3.4H_2O$, and $HNO_3.15H_2O$—*vide* sulphuric acid. S. Arrhenius gave —1362 cals. for the **heat of ionization** with $0{\cdot}1N$-HNO_3 at 35°, for $v=10$; and J. Petersen, —2800 cals. for $u=1{\cdot}5$ to 6·0. W. Bein obtained 0·172 for the **transport number** of the anion of nitric acid in $0{\cdot}05N$-soln. at 25°; H. Jahn and D. Bukschnewsky, 0·170 at 18° with $0{\cdot}00N$- to $0{\cdot}25N$-soln.; and A. A. Noyes and Y. Kato, 0·156 at 20° with $0{\cdot}06N$-soln., and 0·160 in $0{\cdot}007N$- to $0{\cdot}02N$-soln. The NO_3-ion is one of the most electronegative of ions, and its velocity at 18° under a potential gradient of one volt. per cm. is $6{\cdot}18\times10^{-4}$ cm. per second. P. Walden measured the ionic velocities in acetone soln.; and he calculated the diameter of the NO_3'-ion to be $2{\cdot}57\times10^{-8}$ cm. R. T. Lattey discussed the application of the dilution law. V. H. Veley and J. J. Manley concluded from their observations on the electrical conductivity that there is no simple substance of the composition represented by the formula HNO_3; *the substance represented by the formula* HNO_3 *is an ideal because it is really a mixture of* HNO_3, N_2O_5, *and* H_2O. For the affinity constants, *vide* sulphuric acid.

M. Faraday found that a very conc. soln. of nitric acid is a good conductor and, on electrolysis, develops oxygen at the anode, while in the vicinity of the cathode, the liquid is coloured first yellow and then red. If the acid be diluted with more than its own vol. of water, hydrogen is also given off at the cathode, and this the more, the less the concentration of the acid. "The acid which gave no gas at the cathode with a weak voltaic battery did evolve gas with a stronger; and that battery which evolved no gas there with a strong acid, did cause evolution with an acid more dilute." The amount of oxygen liberated by conc. and dil. acids corresponds with the readings of the coulombmeter, and likewise also the acid if it has a sp. gr. below 1·24. C. F. Schönbein, and E. A. Bourgoin found that with a very dil. acid some nitrogen, nitrous acid, and ammonia are formed at the cathode, and E. A. Bourgoin later observed the formation of nitrous oxide and hydroxylamine. Analogous observations were made by T. Bloxam, C. Luckow, G. Vortmann, P. A. Favre, and A. Brester. The nature of the products obtained by the electro-reduction of nitric acid naturally depends on the temp., concentration of soln., degree of acidity, nature of electrode, current strength, and potential. W. Zorn obtained only hyponitrites (*q.v.*) when using a mercury cathode; and K. Ulsch, ammonia, with a copper cathode. E. Müller and co-workers obtained nitric oxide at the cathode during the electrolysis of 40 per cent. nitric acid containing 1 per cent. of nitrous gases in soln. According to H. J. M. Creighton, when a soln. of nitric acid is electrolyzed in a cell in which the anode and cathode are separated by a porous diaphragm, conc. of the acid occurs through electrolytic decomposition of water, and at the same time the conc. of the acid in the anolyte is increased at the expense of that in the catholyte on account of the different migration velocities of the hydrogen and nitrate ions. The acid in the catholyte is further reduced by reduction to nitrogen oxides, hydroxylamine, or ammonia, according to the nature of the cathode metal. Experiments were made in which 70–71 per cent. nitric acid was electrolyzed in a diaphragm cell using platinum electrodes, and provision was made for returning the gaseous nitrogen oxides formed in the anode chamber back to the catholyte chamber. With a current of 6 to 8 ampères and an e.m.f. of 3·0 to 6·5 volts, it was found possible thus to increase the conc. of acid in the anode chamber to 99·65 per cent. HNO_3.

J. Tafel found that while nitric acid is reduced only to hydroxylamine (*q.v.*) by mercury or well-amalgamated electrodes, a copper cathode reduces it to ammonia and at the same time has no action on hydroxylamine. A. Brochet and J. Petit studied the electro-reduction of nitric acid by an alternating current. T. H. Jeffery described the electrolysis of nitric acid with a gold anode, and obtained from the anode liquor crystals of aurinitric acid, $HAu(NO_3)_4.3H_2O$. R. Ihle's observations on the **oxidation-potential** of nitric acid have been discussed in connection with nitrous acid (*q.v.*). He found that if the conc. of the nitric acid be expressed by

C per cent. by vol.; and the e.m.f. of the cell Pt | HNO_3 | $ZnSO_4$ | Zn, by *E* volts, the potential of HNO_3 : Pt becomes:

C . .	95·54	76·94	57·70	35·04	15·27	6·30
E . .	2·045	1·999	1·960	1·890	1·746	1·706
Potential .	1·28	1·23	1·19	1·12	0·98	0·94

The calculations are uncertain because of the unknown nature and conc. of the products of the reaction. The presence of nitrous acid lowers the oxidation potential which increases the rate of oxidation. A. Klemenc and R. Schöller measured the conductivity of mixtures of nitrous and nitric acids; and A. V. Saposchnikoff, of mixtures of sulphuric and nitric acids at 25° and found for the sp. conductivity *K*, and sp. gr. *D*:

HNO_3 .	100	90·31	70·69	40·67	12·54	10·68	7·80	0 per cent.
D .	1·5100	1·5670	1·6608	1·7898	1·8807	1·8810	1·8734	1·8380
K .	0·04797	0·05175	0·06592	0·07145	0·09052	0·09547	0·10130	0·01458

H. F. Vieweg found that air bubbled through nitric acid of less conc. than 0·0003*N* acquires a negative charge, and if of greater conc. a positive charge (0·1*N*-$NaNO_3$ unity). H. Wild studied the electrocapillary curves of nitric acid in different menstrua. S. Wosnessensky measured the contact potential of soln. of nitric acid in water and in isoamyl alcohol; and E. Baur also used several other organic liquids in place of this alcohol. W. Wild measured the electrocapillary action of nitric acid in liquid ammonia soln.

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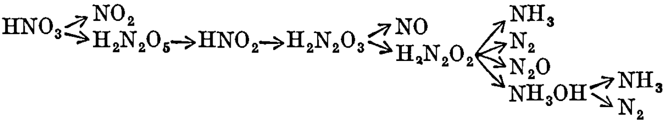
§ 45. The Chemical Properties of Nitric Acid

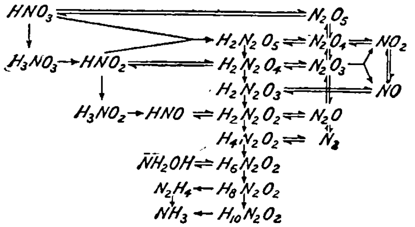
Nitric acid has a peculiar, pungent, and not very powerful smell. It is very corrosive and produces painful wounds on the skin.[1] The burn produced by sulphuric acid is greyish-brown, that produced by nitric acid is bright yellow, and that produced by the mixed acids is reddish-brown with a faint yellow tinge, most distinguishable at the margin of the burn. With more severe burns, there is congestion, and bullæ are quickly formed. As pointed out by J. R. Glauber and R. Boyle, nitric acid gives a bright yellow coloration with hair, wool, wood, etc. Its action on organic matter is rapid. It acts by forming nitric esters or nitro-substitution products. F. C. Calvert said that nitric acid diluted 1 : 1,000 prevents the development of neither fungi nor protoplasmic life.

The electrical conductivity, the lowering of the f.p., the rate of hydrolysis of methyl acetate, and the inversion of cane-sugar, by W. Ostwald[2] have shown it to be one of the most powerful of the monobasic acids. It is therefore very active chemically and it usually behaves as an oxidizing agent, and is itself reduced. S. Genclin described a demonstration experiment to show the reduction of nitric acid to nitrous acid by zinc. The nature of the reduction products depends on the conditions. As previously indicated, there may be produced nitrous acid, nitrogen peroxide, nitric oxide, nitrous oxide, nitrogen, ammonia, hyponitrous acid, and hydroxylamine—and possibly *nitrohydroxylaminic acid*, $H_2N_2O_3$. W. Ostwald has expressed these remarkable results in the language of the ionic hypothesis, by assuming that the simple acid, $(HO)NO_2$, can ionize $HNO_3 \rightleftharpoons NO_2^{\cdot} + OH'$; the hydrate, $(HO)_3NO \rightleftharpoons NO_2H^{\cdot\cdot} + 2OH' \rightleftharpoons NO + 3OH'$; and the hydrate, $(HO)_5N \rightleftharpoons NOH^{\cdot\cdot\cdot\cdot} + 4OH' \rightleftharpoons N^{\cdot\cdot\cdot\cdot\cdot} + 5OH'$. The electrification of the positive ions is supposed to be discharged by the reducing agent. J. J. Acworth and H. E. Armstrong hold that the direct reduction products of nitric acid are nitrous acid, hyponitrous acid, hydroxylamine and ammonia, while nitrogen peroxide, nitric oxide, nitrous oxide, and nitrogen are produced by secondary reactions; thus, for nitrogen peroxide, $HNO_3 + HNO_2 = 2NO_2 + H_2O$; for nitric oxide,

$3HNO_2=2NO+HNO_3+H_2O$; for nitrous oxide, $H_2N_2O_2=N_2O+H_2O$, and $HNO_2+NH_2OH=N_2O+2H_2O$; and for nitrogen, $H_2N_2O_2+2NH_2OH=2N_2+4H_2O$, and $HNO_2+NH_3=N_2+2H_2O$. The special conditions required to secure that one of these products predominates, have been discussed in connection with the particular compounds. L. H. Milligan postulates the existence of G. Oddo's nitrosic or *nitrosonitric acid*, $H_2N_2O_5$—*vide supra*—and assumes the transient formation of A. Angeli's nitrohydroxylamic acid, $H_2N_2O_3$—*vide infra.* He symbolizes the reduction of nitric acid:



V. Schvonen's conclusions are indicated in connection with hydroxylamine. The play of reductions and oxidations, and of hydrations and dehydrations when nitric acid is in contact with the different metals, is thus symbolized by E. J. Joss, where the lines directed vertically downwards represent reductions; and horizontal lines, the gain or loss of water mols.; and the reductions due to hydrogen are assumed to involve hydrogenations by the addition of one or more mols. of hydrogen to a mol. of the compound to be reduced:



The action of heat on the vapour and the decomposition of the soln. during distillation have already been discussed. P. Braham and J. W. Gatehouse said that pure nitric acid is not decomposed during ebullition, but if a trace of nitrous acid be present, decomposition occurs. The vapour of nitric acid is decomposed when passed through a red-hot tube, forming oxygen and nitrogen peroxide, but at a higher temp., E. Mitscherlich showed that nitrogen and oxygen are formed. H. Böttger devised an apparatus for demonstrating the reaction. A. Hantzsch and L. Wolf found that absolute nitric acid is stable at —40°; the 99·5 per cent. acid is unstable at 0°; but the 98·4 per cent. acid can be kept some days at moderate temp. In 1777, C. W. Scheele recorded that nitric acid of sp. gr. not less than 1·4 is decomposed by sunlight whereby the liquid becomes yellow, and oxygen is evolved. J. L. Gay Lussac, J. Fiedler, and W. H. A. Peake confirmed this fact. According to M. Berthelot, the reaction: $4HNO_3=2N_2O_4+2H_2O+O_2$, which takes place when nitric acid is exposed to light is endothermal; and it does not take place in dil. soln. A soln. of sp. gr. 1·365 corresponding with 60 per cent. acid underwent no appreciable change during several weeks' exposure. W. C. Reynolds and W. H. Taylor obtained evidence of a slow decomposition even with 10 per cent. acid. C. F. Schönbein observed that nitric acid of sp. gr. 1·35 in darkness is decomposed at 0° if in presence of platinum black. V. H. Veley and J. J. Manley suggested that the decomposition in sunlight is rather a decomposition of the vapour than of the liquid. P. Braham and J. W. Gatehouse reported:

> Pure nitric acid placed in a full bulb, sealed, and exposed several days to sunlight, remained colourless, and without evolution of gas; but the same acid exposed to sunlight in a sealed tube only partially full was powerfully decomposed, yielding over 1 per cent. of

nitrous acid and a considerable amount of gas. This action in sealed tubes is not continuous; for when the nitrous acid formed attains to about 2 per cent. of the quantity of nitric acid present, all decomposition ceases. This dissociation by sunlight is due to the violet end of the spectrum, the red end having no effect whatever.

This result was confirmed by W. C. Reynolds and W. H. Taylor, who showed that no decomposition occurs if the vapour be screened from light. They also found that M. Berthelot's statement that the reaction is not wholly reversible is inaccurate. The reaction is reversible because the products of the decomposition slowly recombine in the dark. M. Berthelot was probably misled by the slowness of the reverse reaction. The reaction is represented: $4HNO_3 \rightleftharpoons 2H_2O + 2N_2O_4 + O_2$, but it is probable that the decomposition takes place in stages involving first the production of nitrous acid and oxygen, and the nitrous and nitric acid then produce water and nitrogen peroxide. Samples of acid with 70 and 90 per cent. HNO_3 remained colourless if stored many weeks in sealed tubes in darkness, but the 100 per cent. acid remained colourless for a few weeks, while in 12 months, the acid was bright yellow and the tube had developed an oxygen press. of 9·7 atm. With the pure acid, in darkness, there is an induction period occupying about a month, the reaction then proceeds slowly, and after many months, reaches a state of equilibrium. The difference between absolute nitric acid and conc. soln. of that acid may be due to the presence of a trace of nitrogen pentoxide in the vapour, since A. V. Saposchnikoff, and V. H. Veley and J. J. Manley have shown that a measurable amount of the pentoxide is present in the vapour over nitric acid with an excess of sulphuric acid. On the other hand, mixtures of equal vols. of purified nitric and sulphuric acids have been kept nine months in darkness without change of colour or the liberation of any oxygen. M. Berthelot found that radium rays decompose the acid in the same way as sunlight does.

A. F. de Fourcroy said that **hydrogen** does not affect nitric acid at ordinary temp., but when hydrogen mixed with the vapour of the acid is transmitted through a red-hot tube, there are detonations attended by the formation of nitrogen. M. Berthelot also showed that at ordinary temp. and at 100°, free hydrogen does not decompose the acid. F. Kuhlmann found that a mixture of hydrogen and nitric acid vapour forms ammonia when passed through a red-hot tube containing spongy platinum. The so-called nascent hydrogen, however, will reduce the acid, forming products which vary with the conc. of the acid—*vide* ammonia, and other lower oxides formed by the reduction of nitric acid. If the acid is very dilute, E. A. Bourgoin, and J. H. Gladstone and A. Tribe found that it is not much affected by nascent hydrogen. J. H. Gladstone and A. Tribe, and M. N. and S. C. Banerjee found that the conc. acid is rapidly reduced by hydrogen occluded by platinum or palladium; while T. E. Thorpe, and J. H. Gladstone and A. Tribe found that nitrates are reduced to ammonia by the copper-zinc couple, and that reduction is electrolytic, for it takes place at the surface of the copper. According to C. F. Schönbein, nitric acid which can be distilled without the formation of nitrogen peroxide, gives ruddy fumes of that gas when heated in the presence of platinum black, and as indicated above this agent favours the decomposition of the acid in darkness. According to W. R. E. Hodgkinson and F. K. S. Lowndes, when a small hydrogen flame—from platinum tube 9 to 10 cms. long, with a jet about 1 mm. bore —is lowered into a half-litre flask, containing conc. nitric acid, and the press. so arranged that the flame just touches the acid, the jet becomes heated to whiteness, and a fine coloured conical flame extends from the neck of the flask to the liquid surface, and white fumes of ammonium nitrate or nitrite escape. If the white-hot point of the tube be immersed under the acid, red fumes escape as well. The hydrogen continues to burn under the acid until it becomes considerably diluted. P. T. Austen said that hydrogen burns with an intense white flame in the vapour of nitric acid. H. Gall and W. Manchot said that the catalytic reduction of nitric acid in aq. soln. in the presence of spongy platinum yields ammonia and nitrous acid. If **water** be gradually added to the fuming acid, the reddish-brown colour changes to green, then blue, and finally it becomes colourless; if, on the other hand, the fuming acid be added to water, these colours are obtained in their reverse order. L. Marchlewsky considers that the concentrated reddish-brown acid contains nitrogen peroxide, which on the addition of water decomposes into nitrous and nitric acids, that the green colour is due to the presence of both nitrogen peroxide NO_2, and nitrogen trioxide; and that the blue acid contains the trioxide (*vide supra*).

According to H. Moissan,[3] if **fluorine** be passed into nitric acid, each bubble of gas is attended by the decomposition of acid accompanied by a flame. A. Connell found that if **iodine** be gently heated with conc. nitric acid, iodic acid is produced with the liberation of nitrogen peroxide. L. H. Angus and H. M. Dawson found that the effect of nitrates on the solubility of iodine in water can be represented by $S=S_0e^{-0{\cdot}0533C}$, where S_0 denotes the solubility of iodine in water alone in millimols per 1000 grms.; S, the solubility in a salt soln. containing C mols of salt per 1000 grms. of water. For the effect of nitrates on the solubility of iodine in $1{\cdot}3N$-HNO_3 in place of water, $S=S_0e^{-0{\cdot}0577C}$; and in $2{\cdot}7N$-HNO_3, $S=S_0e^{-0{\cdot}0593C}$. A. W. Hofmann confirmed this observation—*vide* iodic acid (2. 19, 11). For the action of **hydrochloric acid** on nitric acid, *vide infra*, aqua regia. G. Gore, and O. Ruff and K. Stäuber investigated the action of nitric acid on **hydrofluoric acid**, but obtained no nitrosyl fluoride (*q.v.*). P. T. Austen said that **hydrogen chloride** does not react with the vapour of nitric acid. C. F. Schönbein found that **hydrogen bromide** decomposes conc. nitric acid at 0°, forming bromine, nitrogen peroxide, and water, and if the soln. be diluted with an excess of water, the original substances are reproduced. P. T. Austen said that hydrogen bromide is only slightly decomposed by the vapour of nitric acid. A. W. Hofmann described the action of nitric acid on **hydrogen iodide** whereby nitric oxide, iodine, and water are formed; with the fuming acid, each bubble of hydrogen iodide produces a red flame with the separation of iodine; P. T. Austen also found that hydrogen iodide reacts with the vapour of nitric acid liberating iodine. A. Eckstädt found that in dil. soln. **hydriodic acid** reduces nitric acid to nitrous acid. R. Luther and N. Schiloff represented the reaction with nitric acid, zinc, and hydriodic acid, $HNO_3+Zn=ZnO+HNO_2$, and $2HNO_2+2HI=I_2+2NO+2H_2O$, as an induced or a coupled reaction, where nitric acid is the actor, zinc the inductor, and hydriodic acid the acceptor. The coupled reactions are linked by an intermediate stage of the actor, which, in the second stage, and so far as it itself is concerned, reacts in a similar manner with the acceptor. In the electrolysis of an acid soln. of a nitrate, the current acts as the inductor, $HNO_3+E=HNO_2$, and the process was therefore called *electrolytic induction*.

Nitric acid transforms **sulphur** into sulphuric acid, and this the more readily the more finely divided the element. According to R. Bunsen,[4] finely-divided sulphur as it separates from the metal sulphides by treatment with acids, may be easily and completely oxidized by the action of conc. nitric acid on a water-bath; with boiling nitric acid of sp. gr. 1·42, the particles of sulphur melt, and coalesce into drops, which are oxidized but slowly. J. J. Berzelius found that **selenium** is converted into the dioxide when warmed with nitric acid; and D. Klein and J. Morel showed that finely-divided **tellurium** is attacked by nitric acid of sp. gr. 1·25, at −11°, when the soln. is diluted with water, tellurous anhydride is deposited, or, at a low temp., tellurous acid, and a basic tellurous nitrate in soln. A. Vogel, and N. A. E. Millon found that nitric acid freed from nitrogen peroxide is not decomposed by **hydrogen sulphide** at ordinary temp. Similarly, R. Kemper passed hydrogen sulphide into nitric acid of sp. gr. 1·18 without decomposition; if the acid contains a trace of nitrogen peroxide, acquired by standing in air, there is a reaction at 25°, and sulphur, sulphuric acid, nitric oxide, nitrogen, and ammonia are formed J. F. W. Johnston, and C. Leconte also noticed that ordinary dil. nitric acid is reduced by hydrogen sulphide, forming sulphur, ammonium sulphate, nitric oxide, and free sulphuric acid. If the conc. acid be poured into a jar of hydrogen sulphide, a blue flame develops at the mouth of the jar in a few seconds, and there is a slight noise. Red fumes appear, and the hydrogen and part of the sulphur are oxidized, and some sulphur separates in the free state. P. T. Austen also observed that hydrogen sulphide burns with a yellow flame in the vapour of nitric acid, forming clouds of nitrosulphonic acid. J. Kessel observed that the reaction with fuming nitric acid is sometimes accompanied by an explosion. A. W. Hofmann observed that fuming nitric acid reacts with incandescence with hydrogen sulphide, and with **hydrogen selenide.** According to S. L. Dana, if dil. nitric acid be repeatedly saturated with **sulphur dioxide,** sulphuric acid is formed. According to R. Weber, nitric acid is not reduced by sulphur dioxide so readily as is nitrous acid. If one vol. of nitric acid, sp. gr. 1·4, be boiled with 5 vols. of **sulphurous acid,** nitrous and nitric oxides are formed ; if less water be used, much nitric oxide is given off before the liquid boils. The reduction of nitric acid occurs more readily in the presence of sulphuric acid. If nitric acid be sufficiently dilute not to be attacked by sulphur dioxide, it is attacked if sulphuric acid be present. The reaction occurs in different ways dependent on the conc. of the acid. Thus, if sulphur dioxide be passed into a mixture of sulphuric acid with 10 per cent. of conc. nitric acid, and the mixture be allowed to stand for 24 hrs., crystals of nitroxyl sulphonic acid are formed. If the crystals are dissolved, and more sulphur dioxide be introduced, the soln. acquires a dark violet colour, which is retained in an atm. of sulphur dioxide. The soln. contains a mixture of nitrous and sulphurous acids. When a mixture of nitric acid and sulphuric acid of sp. gr. at least 1·34, is treated with sulphur dioxide, nitric oxide is formed. If 30 c.c. of sulphuric acid of sp. gr. 1·396 be mixed with 5 to 6 c.c. of nitric acid of sp. gr. 1·25, and treated with sulphur dioxide, in the cold, nitric oxide is given off as the soln. becomes green. With more conc. sulphuric acid, say sp. gr. 1·44 to 1·496, the mixture becomes blue ; with sulphuric acid of sp. gr. 1·53, grass-green to yellowish-green ; and with the acid of sp. gr. 1·63, yellow or colourless. F. Sestini observed that if liquid sulphur dioxide be treated with the hydrate of nitric acid, red vapours and crystals of nitroxylsulphonic acid are formed, which disappear with an excess of sulphur dioxide. The liquid then becomes violet. D. Klein and J. Morel found that hot nitric acid of sp. gr. 1·35 dissolves **tellurium dioxide,** forming a soln. of basic tellurium nitrate. The dehydrating influence of **sulphuric acid** on nitric acid, and the physical properties of the mixed acids, have already been discussed.

P. T. Austen [5] found that **ammonia** burns with a yellow flame if it issues from a fine jet into the vapour of nitric acid, and is ignited ; he also found that the vapour of nitric acid does not support the combustion of **nitrous oxide,** but dense fumes of ammonium nitrate may be formed. Nitric acid absorbs **nitric oxide** more copiously, the more conc. the acid, and the lower the temp. J. Priestley observed that when the conc. acid absorbs nitric oxide, its colour becomes first yellow, then orange, then olive-green, light green, and lastly, greenish-blue. The vol. of the acid increases during the absorption, and red fumes of nitrogen peroxide are formed. According to L. J. Thénard, nitric acid of sp. gr. 1·115 absorbs but little nitric oxide at ordinary temp., and remains colourless ; an acid of sp. gr. 1·32 becomes green ; and acid of sp. gr. 1·41, orange ; and one of sp. gr. 1·5, becomes dark red, and evolves nitrogen peroxide when heated. J. Fritzsche found that dil. nitric acid (1 : 5), say $HNO_3 : 2H_2O$, at 0° forms a blue liquid when treated with nitric oxide, and the liquid furnishes nitrous acid when distilled, if a more conc. acid be used, the liquid is yellow and it contains nitrogen peroxide. V. H. Veley showed that the reaction $2NO + HNO_3 + H_2O \rightleftharpoons 3HNO_2$ is reversible ; and A. V. Saposchnikoff investigated the reaction in some detail—*vide supra,* nitrous acid, and *vide infra,* nitratosulphuric acid. For the action of **nitrogen peroxide,** *vide supra.* A. A. Kasaneeff studied the effect of the acid on the solubility of some nitrates.

According to C. Wittstock,[6] when nitric acid, of sp. gr. 1·2, is warmed with **phosphorus,** nitrous and nitric oxides and a small quantity of free nitrogen are evolved, while phosphorus and phosphoric acids are formed. L. Gmelin said that no nitrous oxide is here produced ; and G. Watson, a colourless gas either nitrogen or in most cases nitrous oxide is produced. L. A. Buchner said that no ammonia is formed during this reaction; but J. Personne found that ammonia is always produced when phosphorus is treated with conc. or dil. (1 : 2) nitric acid. E. J. Maumené obtained a similar result; and C. Montemartini showed that with an excess of 17·3, 28·3, and 68 per cent. nitric acid, at 13° to 14°, the dissolution of one gram of phosphorus causes the production of 0·0739, 0·0824, and 0·0095 grm. of ammonia respectively. C. F. Schönbein observed that conc. nitric acid effervesces violently with phosphorus at ordinary temp., and the action increases in violence until it reaches the ignition temp. of the phosphorus, which then burns in the acid vapours with great splendour. According to L. V. Brugnatelli, paper moistened with nitric acid and laid on a flat piece of phosphorus detonates when struck by a hammer. A. Schrötter said that red phosphorus is more easily oxidized by nitric acid than yellow phosphorus; and J. Böeseken observed the formation of about equal parts of phosphoric and hypophosphoric acids when red phosphorus is boiled with nitric acid of sp. gr. 1·25. A. Siemens found that phosphorus pentoxide is produced when a soln. of yellow phosphorus in benzene is treated with dil. nitric acid, and the solvent volatilized; with red phosphorus, the reaction is more complex. P. T. Austen said that phosphorus inflames in the vapour of nitric acid, and burns with an intense white light. T. Graham found that **phosphine** is violently decomposed by conc. nitric acid; and, added A. W. Hofmann, when a glass rod dipped in fuming nitric acid is held over the water from which phosphine, which is not spontaneously inflammable, is bubbling, each bubble of gas coming in contact with the phosphine causes inflammation. Warm fuming nitric acid dropped in a cylinder of the same gas produces a detonation. H. Davy found that **phosphorous acid** is oxidized by nitric acid to phosphoric acid. H. Rose said that **phosphoric oxide** dissolves in dil. nitric acid more rapidly than phosphorus itself, while J. Pelouze found that conc. nitric acid inflames phosphoric oxide.

N. A. E. Millon[7] found that nitric acid, if free from nitrous acid, does not act on **arsenic** or **antimony** at 20°—only the most conc. acid acts slightly on antimony without effervescence. According to J. L. Proust, when conc. nitric acid is poured on melted **bismuth,** the metal becomes incandescent. N. A. E. Millon showed that bismuth retains its metallic lustre at 20° in dihydrated nitric acid free from nitrous acid; and that bismuth is rapidly dissolved in acid with 4 to 4·5 mols of water, but is not attacked by an acid of sp. gr. 1·108. In the latter case the reaction is started by raising the temp., or by passing in a current of nitric oxide, but it can be again arrested by cooling or by the addition of ferrous sulphate—*vide* arsenic, antimony, and bismuth. C. W. G. Nylander found that with **arsenic trioxide,** and warm nitric acid of sp. gr. 1·38, nitrogen peroxide is evolved; and, added N. Bunge, if the acid is less conc. nitric oxide is formed. C. W. Hasenbach said that nitrogen peroxide alone is formed with an acid of sp. gr. 1·5; and with an acid of sp. gr. 1·38 to 1·40, a dark green mixture of nitrous acid and nitrogen peroxide is produced. Observations on this subject were made by A. Geuther, O. N. Witt, and G. Lunge—*vide supra,* nitrogen trioxide. A. Klemenc and R. Schöller studied the reaction $H_3AsO_3+HNO_3 \rightleftharpoons H_3AsO_4+HNO_2$. They assume that the oxidation occurs through the formation of what they called *E*-nitric acid, $H_2N_3O_3$—*vide infra*—and that there is the cycle of changes $H_3AsO_3+H_2N_3O_8 \rightleftharpoons H_2AsO_4+H_3N_3O_7$; and $H_2N_3O_7+HNO_3 \rightleftharpoons H_2N_3O_8+HNO_2$. The latter reaction is strongly catalyzed by mercury ions. A. Klemenc and F. Pollak found that 10^{-9} mol of mercuric nitrate per litre slows down the velocity of oxidation—*vide* arsenic acid, and arsenic sulphide. H. Wurtz found that **arsenic trichloride** is converted into arsenic acid by nitric acid, while **antimony trichloride** is converted incompletely and with difficulty into antimonic acid—the reaction was studied by S. Schlesinger.

L. Carius,[8] A. Scott, R. J. Friswell, W. Luzi, and others have studied the action of nitric acid on **carbon** and graphite—*vide* **5**. 39, 11. L. R. Parks and P. C. Bartlett studied the adsorption of nitric acid by charcoal; and N. Schiloff and S. Pewsner the adsorption force between charcoal and nitric acid. M. J. M. Creighton and

W. H. Ogden found that in the explosive disintegration of carbon anodes in nitric acid, the gas evolved is mainly air ; the fragments are sometimes covered with minute yellow crystals ; and it is suggested that the disintegration is caused by the formation and decomposition of graphitic acid. Ignited charcoal burns vividly in contact with conc. nitric acid, but the diamond is not oxidized by boiling nitric acid. C. F. Schönbein said that powdered carbon decomposes conc. nitric acid in the cold with the evolution of carbon dioxide and nitrogen peroxide. Glowing carbon was found by P. T. Austen to burn in the vapour of nitric acid, and F. C. G. Müller found the products of combustion of charcoal in nitric acid vapour over 1000° were 52·2–57·2 per cent. CO_2 ; 13·3–14·7, CO ; 3·4–4·6, H_2 ; 24·9–26·7, N_2 ; and some ammonia. M. Dubinin studied the adsorption of nitric acid by charcoal. K. J. P. Orton and P. V. McKie found that **acetylene** is readily absorbed by nitric acid, and with fuming nitric acid carbon dioxide and trinitro methane are produced. The reaction is accelerated by the presence of mercury salts. A. Baschieri, and G. Testoni and L. Mascarelli obtained a number of complex substances. P. V. McKie represented the course of the reaction : $CH:CH \rightarrow CH(OH):CH(NO_2) \rightarrow CH(OH)_2.CH(NO_2)_2 \rightarrow CH(NO_2).CHO \rightarrow CH(NO_2)_2.COOH \rightarrow CH_2(NO_2)_2 \rightarrow C(NO_2)_2:N.OH \rightarrow CH(NO_2)_3$. P. V. McKie observed a similar reaction with **ethylene,** and she obtained β-nitroethyl alcohol among the intermediate products. The course of the reaction is assumed to be: $CH_2:CH_2 \rightarrow CH_2(OH):CH_2(NO_2) \rightarrow CH_2(NO_2).CHO \rightarrow CH_2(NO_2).COOH \rightarrow CH_3.NO_2 \rightarrow CH(NO_2):N.OH \rightarrow CH_2(NO_2)_2 \rightarrow C(NO_2)_2:NOH \rightarrow CH(NO_3)_3$. Nitric acid reacts with numerous **organic compounds,** forming nitro-derivatives; and with **alcohols,** it produces esters. R. Scheidewind removed nitric acid from soln. in certain analytical work by adding alcohol from time to time to the boiling soln. N. Schiloff and co-workers studied the partition of nitric acid between alcohol and water. Nitric acid is quite soluble in **ether,** so that the acid can be extracted from its aq. soln. by this solvent. C. Tanret, P. N. Pavloff, A. Klemenc and R. Schöller, and P. Bogdan measured the partition coeff. of nitric acid between water and ether at 25°. They found that the nitration of organic substances in water and ether soln. proceeds only in the presence of oxides of nitrogen with the nitrogen having a lower valency than five, and is accompanied by oxidation so that the action is autocatalytic. The velocity of nitration varies with the two-thirds power of the conc. of the nitric acid. It is suggested that what they call *E*-nitric acid, $H_2N_3O_8$ is formed $2HNO_3+NO_2 \rightleftharpoons H_2N_3O_8$, as an intermediate compound—*vide supra et infra*, arsenious acid, and the metals. Expressing the concentration of the soln. in mols per litre, P. Bogdan found :

Aq. phase .	0·02462	0·02760	0·04749	0·09005	0·2644	0·4811	0·578	50·9145
Ether phase .	0·0$_3$249	0·0$_3$290	0·0$_3$641	0·0$_2$181	0·0$_2$894	0·0278	0·0378	0·0855

He also observed that the solubility of water in ether is influenced by the presence of nitric acid in dil. soln. The mol. elevation of the b.p. of ether produced by nitric acid is not independent of the conc. The conductivities of soln. of nitric acid in water saturated with ether show that the degrees of ionization calculated from them are in agreement with the dilution law, and the calculated ionization constant, at 25°, is 1·39. Assuming that mass law is true for the ionization of nitric acid in the ether soln., the coeff. of partition of the non-ionized part of the nitric acid is water : ether=3·9. According to A. Quartaroli, the reaction between anhydrous **formic acid** and nitrates is really a process of autocatalysis in which nitrogen trioxide is the positive catalyst. Until a trace of this substance has been formed, the velocity of the reaction is very small, but the nitrogen trioxide cannot accumulate in quantity, because it also reacts with formic acid. In agreement with this view it is found that oxidizing agents, transforming the nitrogen trioxide into nitric acid, act as negative catalysts. Traces of potassium chlorate, hydrogen dioxide, potassium permanganate, or carbamide hinder the reaction or prevent it entirely, so that there results the paradox that oxidizing agents may prevent oxidation. Nitrates are reduced by quickly warming them with formic acid : $2KNO_3+6HCOOH=4CO_2+5H_2O+2HCOOK+N_2O$, the reaction is quantitative and can be used for quantitative determinations ; the reaction is also a convenient method of preparing nitrous oxide free from other nitrogen oxides provided the heating be rapid until the first bubbles appear. If the initial warming be slow, the soln. becomes blue and red fumes appear. **Formaldehyde** can be used in the preparation of fuming nitric acid. When paraformaldehyde is added to nitric acid, nitric oxide, NO, is evolved even in the cold. By gently heating and conducting the escaping gases with nitric acid, the fuming acid is obtained. F. O. Rice emphasized the parallel behaviour in the nitration of **phenol** by nitric acid, and the action of metals on that acid. With dil. nitric acid, 25 per cent. of the acid may be reduced to nitrous oxide and nitrogen during the nitration of phenol ; and by keeping the temp. below 100°, much of the reduction of the acid to lower oxides can be avoided. K. H. Meyer and co-workers, and A. Klemenc and E. Ekl studied the action of nitric acid on phenol and on aryl-compounds. The action of nitric acid on metals in likened by N. R. Dhar to the action of the acid on organic compounds like sugar, starch, etc. Here, as shown by A. Naumann, the reaction, as in the conversion of sugar to oxalic acid, is accelerated by vanadium pentoxide, as well as by sodium nitrate, and manganese salts, whereas molybdic acid and silver salts retard the action. O. Warburg studied the reduction of nitric acid in the cells of the *Chlorella vulgaris*, in light and in darkness ; and S. G. Mokruschin, the adsorption of the acid by filter paper. C. M. Faber and co-workers studied the adsorption of nitric acid by colloidal **silica** (*q.v.*) ; and N. R. Dhar, the induced reaction involving the effect of nitric acid on the reduction of mercuric chloride by oxalic acid. For the reducing action of **titanous salts,** *vide infra.*

In 1663, R. Boyle [9] noticed that many **metals** remain inert towards conc. nitric acid, but are readily attacked by the dil. acid. This observation was confirmed in 1685 by J. Bohn, by J. Woodhouse in 1799, and by J. Keir in 1790. According to J. L. Proust, during the attack of the metals by nitric acid, oxygen is transferred to the metal with the evolution of heat. The action is slow at first, but becomes accelerated, and sometimes ends in actual combustion or incandescence such as occurs when conc. nitric acid is poured on heated iron filings, or on melted bismuth, tin, or zinc. N. A. E. Millon's memoir : *Recherches sur l'acide nitrique*, is one of the most important—*vide* **3.** 21, 6—he demonstrated that nitric acid of whatever concentration does not attack many metals ; the reaction occurs only when a trace of free nitrous acid is present. This important result was confirmed by V. H. Veley, W. J. Russell, S. W. Young and E. M. Hogg, etc. V. H. Veley inferred from his observations that (i) the primary change is that between the metals and nitrous acid ; (ii) no gas is evolved at first from the surface of the metal ; (iii) the amount of nitrous acid increases up to a constant and maximum proportion ; and (iv) those conditions which increase the amount of metal dissolved per unit time, are equally those conditions which increase this constant proportion of nitrous acid. If then a trace of nitrous acid becomes once formed, and if, also, the quantity of nitric acid is present in very considerable excess, it would appear that these results may be explained as follows : (i) the metal dissolves in nitrous acid to form the metallic nitrite and nitric oxide ; (ii) the nitrite formed is decomposed by the excess of nitric acid to reproduce the nitrous acid ; and (iii) the nitric oxide formed in (i) is not evolved as such, but reduces the nitric acid or the nitrate to produce a further quantity of nitrous acid. These changes may be presented thus, taking copper for example: (i) $Cu+4HNO_2=Cu(NO_2)_2+2H_2O+2NO$; (ii) $Cu(NO_2)_2+2HNO_3=Cu(NO_3)_2+2HNO_2$; (iii) $2NO+HNO_3+H_2O=3HNO_2$. G. J. Burch and V. H. Veley found that when the metals, copper, silver, bismuth, and mercury are introduced into purified nitric acid of varying degrees of concentration, and a couple made with platinum, the electromotive force of such a cell increases considerably until it reaches a constant and (in most cases) a maximum value. This rise of electromotive force is attributed to the production of nitrous acid by the decomposition of the nitric acid, and the final value is considered to be due to the former acid only, while the initial value is due for the most part to the latter acid, though it is affected to a remarkable degree by the amount of impurity of nitrous acid either initially present or produced by minute and unavoidable uncleanliness of the metallic strips and the containing vessel. If nitrous acid has been previously added to the nitric acid, then the maximum electromotive force is reached at once. If the conditions, namely, increase of temp., impurity, and of concentration of acid, are such as could favour a more rapid production of nitrous acid, then the rise of electromotive force is concomitantly more rapid. Conversely, if the conditions are unfavourable to the production of nitrous acid, the rise of electromotive force is less rapid. If any substance, such as urea, be added, which would tend to destroy the nitrous acid as fast as it may be formed, then the rise of electromotive force is extremely slow, being dependent upon the number of molecular impacts of nitrous acid upon the surface of the metal. Thus the results obtained by the electrometer and by the chemical balance are in every way confirmatory, the one of the other. R. Ihle did not agree with these conclusions. If the rate of increase in the e.m.f. depends solely on the number of nitrous acid mols. formed from the nitric acid, the maximum e.m.f. finally attained should be greater the greater the conc. of the nitrous acid in the nitric acid. The opposite of this is true, and to get over the difficulty, G. J. Burch and V. H. Veley assumed that the ready-formed nitric acid is not so active as nitrous acid in the process of formation and decomposition. W. D. Bancroft added that the assumption that the metal dissolves to nitrite has no weight because the addition of nitrous acid to Grove's cell, or Smee's cell—1. 16, 5—increases the depolarizing action of the nitric acid, but no metal dissolves in the nitric acid soln. and consequently there is no formation of nitrite. According to R. Ihle:

> If one dilutes the conc. nitric acid in the Grove cell gradually and measures the e.m.f. of the cell at the same time, one finds that the e.m.f. remains nearly constant until the conc. of the nitric acid drops to about 38 per cent. At slightly lower conc. the cell shows, though at first only for a very short time, a changed and much smaller e.m.f. than the 1·8 volt characteristic of the Grove cell; it corresponds rather to the 0·7 volt of the Smee cell. If one dilutes the nitric acid more and more, the time during which the cell stays at the lower potential increases until at a nitric acid content of 27–28 per cent. the element keeps the low e.m.f. of the Smee cell permanently. Just as one can make dil. nitric acid active as a depolarizer by means of nitrous acid, so one can also remove the depolarizing power of conc. nitric acid containing more than 38 per cent. HNO_3, by removing continuously the small amount of nitrous acid which is always present in so strong nitric acid by means of urea or potassium permanganate and can thereby convert a Grove cell into a Smee cell. With very conc. acid containing 50–60 per cent. HNO_3, the conversion is only temporary because more nitrous acid forms soon. From this it follows that nitrous acid is the real depolarizer in the Grove cell and not nitric acid as is usually assumed, or at any rate, that it is only in presence of nitrous acid that the oxygen of the nitric acid reacts with hydrogen set free electrolytically at the platinum. The question arises as to how this action takes place, and it seems probable that we are dealing with a case of catalysis. Nitrous acid plays the part of a catalyzer here just as it does in other cases, such as the action of nitric acid on metals studied by V. H. Veley.

The conc. of the nitrous acid does not increase when a soln. of nitric acid is electrolyzed, even in cases where there is no evolution of gas. If nitric acid were the depolarizer it should be almost entirely removed before the nitrous acid is attacked. In order to explain the removal of nitrous acid, W. D. Bancroft inferred that there is a reversible reaction in which there is a state of dynamic equilibrium, $HNO_3+HNO_2 \rightleftharpoons N_2O_4(\text{or } 2NO_2)+H_2O$, so that nitric acid is continually changing to nitrogen peroxide, and being formed therefrom. During the moments of change, the nitric acid, the nitrogen atom, or some radical containing nitrogen and oxygen must be in a different state from what it would be if no nitrous acid were present and if this reaction were not taking place. The particular intermediate stage involved in this reaction presumably permits more rapid reaction with nascent hydrogen. E. J. Joss inferred that the activation of the nitric acid depends on the formation of nitrosic acid (*q.v*) as an intermediate product in the state of dynamic equilibrium:

$HNO_3+HNO_2 \rightleftharpoons H_2N_2O_5 \rightleftharpoons 2NO_2+H_2O$. Nitrous acid is not the actual depolarizer, but it acts as a catalytic agent making the nitric acid active; the real depolarizer in the action of nitric acid on metals is nitrosic, not nitrous, acid.

Details of the various observations of the action of nitric acid on the metals are discussed in connection with the individual elements. The more important memoirs are those of V. H. Veley, C. Montemartini, E. Divers, H. E. Armstrong and J. J. Acworth, E. J. Joss, W. D. Bancroft, G. O. Higley and co-workers, and J. L. Schönn. B. C. Banerji and N. R. Dhar studied the action of nitric acid on metals in the presence of different salts. Ferrous salts acted as catalysts by producing nitrous acid in a reaction with nitric acid; ferric salts also acted as catalysts by being reduced to ferrous salts by the metal. Oxidizing agents like potassium permanganate and chlorate act as negative catalysts by hindering the formation of nitrous acid. The dissolution of a 1 : 1 nickel-copper alloy is periodic because a period of activity is followed by one of no activity, and that again by one of activity, and so on, continuously alternating in sequence. This *pulsating action* was discussed by M. Faraday, C. F. Schönbein, A. Mousson, L. Gmelin, etc.

The earliest view of the reaction between nitric acid and the metals assumed that the metals are first oxidized by the acid—*the oxidation theory.* Thus, L. Gmelin said that the portion of the nitric acid which oxidizes the metal is sometimes converted into nitrogen peroxide, sometimes into nitric oxide, or into nitrous oxide, or nitrogen gas; and, if the metal at the same time decomposes water, the hydrogen of the water combining with the nitrogen of the acid forms ammonia. As N. A. E. Millon has shown, the oxidation of the metal usually occurs only when nitrous acid is present; because, although nitrous acid contains less oxygen than nitric acid, it parts with that element more readily because its affinity for water is less than that of nitric acid. J. F. Norris, and J. L. Howe favour the oxidation theory. The theory was advocated by N. R. Dhar, who compared that action of nitric acid on metals with that of the persulphates on the metals. This theory is virtually *the phlogiston hypothesis* of C. W. Scheele translated into the language of the antiphlogistic theory.

Another hypothesis—*the hydrogen theory*—assumes that a nitrate of the metal and nascent hydrogen are first formed. The nascent hydrogen is then supposed to reduce the nitric acid to nitrous acid, etc. J. J. Acworth expresses the idea in this form: The action of the metal consists simply in the displacement of the hydrogen of the acid and the formation of the corresponding nitrate in the manner expressed by the equation: $M+2HNO_3=M(NO_3)_2+2H$. In no circumstances, however, is the hydrogen thus displaced evolved as such. It at once acts on the free acid present, or on the metal nitrate which has been formed, reducing it more or less completely to nitrous acid, hyponitrous acid, hydroxylamine, and ammonia; while the nitrogen peroxide, nitric oxide, nitrous oxide, and nitrogen are formed by secondary reactions. This view of the reaction agrees with that of W. D. Bancroft.

The products formed by the action of metals, and metal salts on nitric acid involve reduction, or hydrogenation, dehydration, and hydration processes as previously indicated—also *cf.* the individual elements. C. L. Bloxam found that with sodium *hydrogen* is evolved. The formation of *nitrogen peroxide* was observed by J. J. Acworth, H. E. Armstrong and J. J. Acworth, P. C. Freer and G. O. Higley, C. Montemartini, etc., by the action of many metals—*e.g.* copper, zinc, cadmium, mercury, antimony, bismuth, molybdenum, iron, cobalt, and nickel; and L. H. Milligan and G. R. Gillette, by the action of stannous chloride on nitric acid. The nitrous acid or nitrite is probably formed by direct reduction, and by the action of hydroxylamine. The nitrous acid reacts with nitric acid to form nitrogen peroxide: $HNO_3+HNO_2=2NO_2+H_2O$. As indicated above, E. J. Joss assumed that nitrosic acid, $H_2N_2O_5$ (*q.v.*), represents an intermediate stage in the process: $HNO_3+HNO_2 \rightleftharpoons H_2N_2O_5 \rightleftharpoons 2NO_2+H_2O$. C. Kippenberger, A. van Bijlert, J. Tafel, P. C. Ray, and C. Montemartini observed the production of *nitrites*—or *nitrogen trioxide*—in the reduction of nitric acid by magnesium, zinc, cadmium, mercury, aluminium, lead, antimony, bismuth, molybdenum, manganese, cobalt, and nickel. J. J. Acworth, H. E. Armstrong and J. J. Acworth, P. C. Freer and G. O. Higley, C. Montemartini, A. van Bijlert, A. Pleischl, N. A. E. Millon, F. Kuhlmann, etc., observed *nitric oxide* to be formed by the reducing action of copper, silver, zinc, cadmium, tin, antimony, bismuth, molybdenum, iron, cobalt, and nickel; and L. H. Milligan and G. R. Gillette, by the action of ferrous and stannous chlorides on nitric acid. The nitric oxide is derived from the nitrous acid: $3HNO_2=2NO+H_2O+HNO_3$; and from the ephemeral nitrohydroxylamic acid: $H_2N_2O_3=2NO+H_2O$. J. J. Acworth, H. E. Armstrong and J. J. Acworth, C. Montemartini, etc., observed *nitrous oxide* among the products of the action of copper, zinc, cadmium, cobalt, and nickel on nitric acid. J. J. Acworth observed no nitrous oxide with silver. L. H. Milligan and G. R. Gillette obtained nitrous oxide by the action of stannous chloride. Nitrous oxide is formed by the dehydration of hyponitrous acid: $H_2N_2O_2=H_2O+N_2O$, or by the interaction of nitrous acid and hydroxylamine: $HNO_2+NH_2OH=N_2O+2H_2O$; or $2HNO_3+4NH_2OH=3N_2O+7H_2O$. C. Montemartini found *hyponitrites* among the products of the action of zinc, cadmium, cobalt, and nickel on nitric acid. Hyponitrous acid is formed by direct reduction; J. J. Acworth, H. E. Armstrong and J. J. Acworth, H. St. C. Deville, A. von Bijlert, A. Pleischl, C. Montemartini, etc., obtained *nitrogen* among the products of the action of copper, silver, zinc, cadmium, tin, cobalt, and nickel on nitric acid. L. H. Milligan and G. R. Gillette also observed that some nitrogen is formed when nitric acid is reduced by stannic chloride. It is probable that the nitrogen is not formed by the interaction of nitrous acid and ammonia, since nitrogen is produced when there is nothing to show that any ammonia is formed. As observed by G. Oesterheld, it may be formed by the interaction of hyponitrous acid and hydroxylamine: $H_2N_2O_2+2NH_2OH=2N_2+4H_2O$; and, according to M. Berthelot and J. Ogier, A. Hantzsch and L. Kaufmann, and P. C. Ray and A. C. Ganguli, by the reaction: $5H_2N_2O_2=4H_2O+2HNO_3+4N_2$. E. Divers, C. Montemartini, and C. Kippenberger found that *hydroxylamine* is a product of the action of nitric acid on magnesium, zinc, cadmium, aluminium, tin, and manganese—C. Montemartini, and A. van Bijlert observed none with zinc, and J. Tafel, none with copper, or mercury. J. A. Wilkinson showed that if the conc. of the mercury ions be kept low, then hydroxylamine is formed. E. J. Maumené, O. von Dumreicher, and L. H. Milligan and G. R. Gillette observed hydroxylamine to be a product of the action of stannous chloride on nitric acid; and L. H. Milligan and G. R. Gillette, of titanous chloride. Hydroxylamine is probably produced by direct reduction; so also with *ammonia:* $HNO_3\rightarrow HNO_2\rightarrow H_2N_2O_2\rightarrow NH_2OH\rightarrow NH_3$. T. E. Thorpe, and J. H. Gladstone and A. Tribe observed that the copper-zinc couple will reduce nitrates to ammonia; and E. Divers divided the metals into two classes: (i) those like copper, silver, mercury, and bismuth which formed neither ammonia nor hydroxylamine; and (ii) those which produce hydroxylamine or ammonia. Ammonia was observed with magnesium, zinc, cadmium, aluminium, tin, lead, iron, and sodium amalgam. P. C. Freer and G. O. Higley also observed ammonia with iron; W. Smith, with aluminium; C. Montemartini, with lead; A. Pleischl, with tin; F. Kuhlmann, with zinc; and J. W. Turrentine, and E. J. Joss, with nitrates and copper in the presence of sulphuric acid. J. Tafel obtained no ammonia with mercury or copper; and G. O. Higley found none in the products of the reaction with lead and nitric acid, but E. Divers obtained ammonia, and E. J. Joss said that the reason ammonia is not always obtained, is because the secondary reaction by which an intermediate product decomposes to give nitrous oxide, is catalyzed by lead ions, until it predominates over the direct reduction. J. B. Kinnear obtained a quantitative reduction of nitrates to ammonia by sulphuric acid and zinc. This shows that the reduction potentials of zinc and lead suffice to reduce nitric acid to the ammonia stage. C. Kippenberger observed that dil. soln. of nitrates are reduced to ammonia by magnesium, aluminium, and manganese; J. Personne, and E. J. Maumené, by phosphorus, arsenic, and antimony; and C. Montemartini, by cadmium, cobalt, and nickel. L. H. Milligan and G. R. Gillette found that while stannous chloride can reduce nitric acid to ammonia, the apparently stronger reducing agent carries the reduction to hydroxylamine. The reaction was also examined by E. Divers and T. Haga, S. Schlesinger, and E. Pugh.

A. de la Rive held that the dissolution of a metal in connection with an acid depends on the formation of local elements between an impurity in the metal and the acid, say Cu | HNO_3 | M. H. E. Armstrong amplified the suggestion, and developed *the electrolytic theory* of chemical action. He said that two substances will react only in presence of certain impurities (catalytic agents). Interaction does not take place between pure substances. He assumes that "when the complex formed by the association of the interacting substances meets with the necessary third component, a conducting system is established, and that as soon as this is formed a change sets in. . . ." According to this hypothesis, "a circuit of change must comprise three distinct terms or components." One of these must be a conductor of electricity which is capable of forming with the reacting substance a system analogous with a closed voltaic circuit. As W. D. Bancroft expressed it:

> The most striking characteristic of an electrolytic action is that it occurs in two places—at the anode and at the cathode. This peculiarity can be made less marked by bringing the electrodes nearer and nearer together. When the distance between them vanishes, we have a chemical reaction in the ordinary sense of the word and not an electrochemical reaction. Any chemical reaction, therefore, which can be made to take place electrolytically, must consist of an anode and a cathode process. Considering the matter in this light, we see that there is a possibility of the anode and cathode processes interfering and of one perhaps masking the other.

T. Ericson-Aurén and W. Palmaer found that the addition of anything which raises the e.m.f. of the combination—the addition of certain metal salts, depolarizers, etc., and variations in the nature of the negative element—increases the rate of dissolution, and conversely. This subject has been discussed in connection with copper—**3**. 21, 6. W. D. Bancroft said that the general results show that the action of nitric acid on metals can be profitably considered as a case of electrolytic corrosion, the anode reaction being the formation of a nitrate. The nature of the metal shows itself in three ways: (i) in the reducing power as measured by the over-voltage; (ii) in the catalytic action of the metal; and (iii) in the catalytic action of the salt of the metal. The electrolytic reduction of nitric acid has been discussed in connection with hydroxylamine. The hydrogen and electrolytic theories can be translated into the language of the *ionic hypothesis;* thus, according to W. Ostwald—*vide supra*—the reduction of nitric acid is supposed to start from the ionization of the acid, so that the direct reduction products are nitrogen peroxide, nitrous acid, nitric oxide, hyponitrous acid, and either nitrogen or hydroxylamine and ammonia, with nitrous oxide as a secondary dehydration product of hyponitrous acid—*vide supra* for the relation of these products to nitric acid.

L. S. Bagter, in explaining the action of nitric acid on copper, assumed that nitrous acid is the depolarizer. He concluded that the process involved (i) the oxidation of the hydrogen film on the copper by the nitrous acid, which itself is reduced to hyponitrous acid, the copper passing into soln. to replace the hydrogen removed; and (ii) the oxidation of the hyponitrous acid to nitrous acid by nitric acid, which itself is reduced to nitrous acid. A. Klemenc assumed that in the nitration of organic substances—*vide supra*—what was called *E*-nitric acid, $H_2N_3O_8$, is formed, and the theory can be also applied to the action of nitric acid on the metals. Thus, P. C. Ray's observation that mercurous nitrite is formed by the action of nitric acid on mercury is explained by assuming that a state of equilibrium, $2HgNO_3+NO_2 \rightleftharpoons Hg_2N_3O_8$, is formed in the diffusion layer near the surface of the metal, and that the mercury *E*-nitrate diffuses away and is decomposed: $2Hg_2N_3O_8+H_2O=HgNO_2+3HgNO_3+2HNO_3$. The conc. of the *E*-acid in the diffusion layer reaches a maximum at a distance from the metal of five-sixths of the thickness of the diffusion layer. M. Drapier's observation that the velocity of soln.

of a copper cylinder in nitric acid is considerably lessened by rotating the cylinder is explained by assuming that *E*-acid is lost on the soln. side of the diffusion layer during rotation.

According to J. G. Thompson, aluminium and its alloys are superior in their resistance to 100 per cent. nitric acid to all the iron-alloys tried excepting high-silicon cast-iron; these alloys, however, are severely corroded by acid of less than 68 per cent. HNO_3. Molybdenum steel, or steel containing 5·5 per cent. chromium, was little better than plain steel, but steels with 10·8 to 15·7 per cent. chromium, better resisted attack by the stronger acid; while steels with over 16 per cent. chromium showed no signs of attack by nitric acid below 68 per cent. concentration. The presence of nickel reduces the beneficial action of chromium. Of all the alloys tested, a high-silicon cast-iron—14·55 per cent. Si, and 0·59 per cent. C—was the most resistant. It was unattacked by acid of any concentration. A similar cast-iron with 12·24 per cent. Si, and 1·17 per cent. of C, was not so good.

H. Braconnot showed that an alcoholic soln. of nitric acid is often less active than the aq. soln. He said that the alcoholic soln. acts feebly on bismuth, zinc, and copper because of the low solubility of the nitrates of these metals in alcohol; and that it does not attack mercury because of the insolubility of the nitrate in alcohol. P. Pascal discussed the action of mixtures of sulphuric and nitric acids on aluminium, steel, and lead. The addition of sulphuric or nitric acid to a manganic salt or manganese dioxide, in the presence of hydrofluoric, phosphoric, or arsenic acid, may convert the whole of the manganese into the corresponding manganic salt. J. Jannek and J. Meyer found that conc. nitric acid distilled with **platinum** apparatus contains impurities not found when vessels of fused-quartz are employed. G. P. Baxter and F. L. Grover said that if clean, well-seasoned platinum is used, the results are as good as with quartz provided the acid is free from traces of hydrochloric acid.

The lower oxides of many metals and their salts are oxidized by either cold or hot nitric acid—*e.g.* **cuprous oxide, mercurous oxide, stannous oxide, and ferrous oxide,** and their salts. According to A. von Bijlert,[10] **ferrous sulphate** in the presence of free sulphuric acid is quantitatively oxidized to ferric oxide; but in the absence of sulphuric acid, about one-third of the ferrous salt is oxidized to ferric nitrate: $6FeSO_4+8HNO_3=2Fe_2(SO_4)_3+2Fe(NO_3)_3+2NO+4H_2O$; with dil. nitric acid—230 grms. HNO_3 per litre—there is no action at 0°, a slow action at 25°, and a rapid action at 30°. L. H. Milligan and G. R. Gillette concluded that when an excess of nitric acid, of 15–20 per cent. strength, is reduced at 20° by ferrous salt soln., the reaction first passes through an induction period, and the soln. becomes dark red-brown indicative of the formation of the $Fe^{\cdot\cdot}.NO$ complex which is rapidly decomposed—nitric oxide is the principal product, but considerable nitrogen peroxide is also formed. When small amounts of nitric acid are added to an excess of boiling ferrous salt soln., nitric oxide only is produced. O. Baudisch and P. Mayer found that the reduction of nitrates by ferrous hydroxide in neutral and alkaline soln. is quantitative. The reduction of nitric acid by **stannous chloride** has been discussed in connection with hydroxylamine. M. Coblens and J. K. Bernstein found that nitric acid furnishes nitric oxide when treated with stannous chloride containing a drop of ferrous sulphate; and when an excess of sodium hyposulphite acts on nitric acid. L. H. Milligan and G. R. Gillette concluded that

> When an excess of nitric acid of 10–50 per cent. strength is treated in the cold with stannous salt soln., hydroxylamine salts are the *primary* end-product of the reaction, but when the conditions of temp. and conc. are such that the nitric acid and the hydroxylamine salts react, then nitrous oxide is the chief product together with small amounts of nitric oxide, nitrogen and traces of nitrogen peroxide. No ammonium salts are formed. When stannous salts are used in excess over the nitric acid, the reaction takes place with hydroxylamine and ammonium salts as the products either in hot or cold soln., but the reaction is very slow in the latter case. When an excess of nitric acid is treated with titanous salt soln., the reaction takes place very rapidly with the formation of nitric oxide as the chief

product together with a considerable amount of nitrous oxide, a smaller amount of nitrogen, and traces of nitrogen peroxide and also of hydroxylamine salts. No ammonium salts are formed. The reaction appears to progress in practically the same way no matter whether the nitric acid or the titanous salt is in excess, neither hydroxylamine nor ammonium salts being formed in the latter case. Titanous salts are stronger reducing agents than corresponding stannous salts, and yet the chief product by the former acting on an excess nitric acid is nitric oxide; whereas the chief product from the latter is hydroxylamine, which is a "more reduced" compound, but is produced by the weaker reagent. This shows that catalytic effects play an important part, and evidence indicates that the "ous" salt of titanium is the catalyzer for the decomposition of nitrohydroxylamic acid and production of nitric oxide.

Many **metal chlorides** when heated with an excess of nitric acid are converted into the nitrates. Thus, J. L. Smith found that the transformation occurs with potassium or sodium chloride in the presence of 7 to 8 parts of nitric acid; J. S. Stas said that at 40°–50°, potassium, sodium, or lithium chloride require respectively 3, 4, and 5·5 parts of nitric acid. J. L. Smith said that ammonium chloride and nitric acid yield nitrous oxide. H. Wurtz found that auric, cadmium, cerium, lanthanum, didymium, ferric, and platinic chlorides are decomposed by nitric acid incompletely and with difficulty. S. Schlesinger said that the two copper chlorides, mercurous, zinc, and lead chlorides, are decomposed, but, added H. Wurtz, with difficulty and incompletely; while mercuric and silver chlorides are not attacked. F. Rose found cobalt amminochlorides are readily converted into the nitrate.

Nitric acid is usually monobasic, forming a series of salts, the **nitrates.** The basic salts have been discussed by A. Ditte,[11] E. Groschuff, and others—see, for example, the basic lead nitrates. The nitrates are usually made by the action of the acid on the metal, hydroxide, oxide, carbonate, etc. According to H. Braconnot, the conc. acid does not decompose dehydrated sodium, barium, calcium, or lead carbonate, even when boiling, because the nitrates of these bases are insoluble in the conc. acid, and a surface film of nitrate protects the remainder of the carbonate from the acid. Potassium carbonate is decomposed by the conc. acid because the nitrate is soluble in the conc. acid. J. Pelouze said that an alcoholic soln. of nitric acid does not act on potassium carbonate, but it acts slowly on sodium, barium, and magnesium carbonates, and rapidly on calcium and strontium carbonates; because, added H. Braconnot, calcium and strontium nitrates are readily dissolved by alcohol, whereas potassium nitrate is but sparingly soluble in that menstruum. Potassium hydroxide resists attack by a soln. of nitric acid in ether unless the mixture is boiled or shaken. A. A. Kazantzeff discussed the influence of nitric acid on the solubilities of the nitrates.

The great number of hydrates of the metallic nitrates in which the number of water mols. is some multiple of 3—say 3, 6, 9, 12—has been the subject of remark, and has led observers to assume that these hydrates are to be regarded as addition products of the base with one of the hypothetical nitric acids—orthonitric acid, H_5NO_5, mesonitric acid, H_3NO_4, and ordinary or meta-nitric acid, HNO_3, and also nitric anhydride, N_2O_5. H. E. Armstrong has argued that the acid and base first unite additively, and that the salt is formed by an intra-molecular change in the addition-product so produced. In confirmation, there are many hydrates of salts whose composition can be exactly derived from the direct addition of acid and base; *e.g.* $CaSO_4.2H_2O$; $BaCl_2.2H_2O$; $HgNO_3.H_2O$, etc. According to J. H. Kastle, 75 per cent. of the nitrates described in literature can be included in one or other of the following five classes:

(1) The anhydrous nitrates are addition products of nitric anhydride and the metallic oxide, $Cs_2O+N_2O_5=2CsNO_3$, *e.g.* the nitrates of the five alkali metals, silver, barium, strontium, magnesium, thallium, gallium, and lead; and the double nitrates of gold or silver with the alkali metals: *e.g.* $KAu(NO_3)_4,KAg(NO_3)_2$.

(2) The nitrate is an addition product of ordinary nitric acid, and the metallic base: $Hg(OH)+HNO_3=HgNO_3.H_2O$. Thorium nitrate, $Th(NO_3)_4.4H_2O$, is another example.

(3) Many nitrates of the bi- and ter-valent metals are addition products of mesonitric acid: $Cd(OH)_2+2H_3NO_4=CdNO_3.4H_2O$, and calcium and strontium nitrates, $Ca(NO_3)_2.4H\ O$ and $Sr(NO_3)_2.4H_2O$, are further examples. With the tervalent metals,

$Fe(OH)_3+3H_3NO_4=Fe(NO_3)_3.6H_2O$; and the corresponding nitrates of didymium, thallium, cerium, erbium, lanthanum, samarium, and yttrium are examples. A series of double nitrates of cerium with cobalt, magnesium, manganese, nickel, or zinc, of the type : $2Ce(NO_3)_3.3MgNO_3.24H_2O$; and a series with lanthanum nitrate and magnesium, manganese, or zinc nitrate of the type : $2La(NO_3)_3.3Zn(NO_3)_2.24H_2O$, belong to the same class.

(4) Another series may be derived by the addition of orthonitric acid, H_5NO_5, to the bivalent metal base, with the bivalent metals: $Co(OH)_2+2H_5NO_5=Co(NO_3)_2.6H_2O$, and the corresponding nitrates of nickel, iron, manganese, magnesium, zinc, and calcium. Examples with the tervalent metals are: $Al(OH)_3+3H_5NO_5=Al(NO_3)_3.9H_2O$, and the corresponding nitrates of chromium, and iron, as well as the double nitrates of nickel and didymium, $2Di(NO_3)_3.3Ni(NO_3)_2.36H_2O$. Thallium nitrate is an example with a quadrivalent metal: $Th(OH)_4+4H_5NO_5=Th(NO_3)_4.12H_2O$.

(5) A few nitrates can be referred to a pyrometanitric acid, $H_4N_2O_7$. Thus, $Cu(OH)_2+H_4N_2O_7=Cu(NO_3)_2.3H_2O$; and similarly also with germanium, and manganese nitrates.

J. H. Kastle argued that the hypothesis contains " at least an element of truth." When the hypothesis is adapted to an imaginary $H_{13}N_3O_{14}$, regarded as $3H_5NO_5$ less H_2O, in order to explain the octohydrate of thallium nitrate, $Th(NO_3)_3.8H_2O$, the argument becomes less probable. J. Loewe, and M. E. Chevreul referred some of the basic lead nitrates—*e.g.* $PbHNO_4,Pb_3(NO_4)_2$—to an hypothetical orthonitric acid, while J. H. Kastle suggested the possibility of the hydrated nitrates being salts of more complex acids *e.g.*—$Fe(NO_3)_3.9H_2O$ is $H_{18}FeN_3O_{18}$; and when part of the hydrogen is replaced by a metal, the so-called basic salts are formed.

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§ 46. The Halogen Compounds of Nitrogen

H. N. Warren [1] electrolyzed a conc. soln. of ammonium fluoride, and observed that oily drops collected about the cathode; he suggested that **nitrogen fluoride,** analogous to nitrogen chloride, was formed. The oily drops exploded more violently than nitrogen chloride. O. Ruff and E. Geisel said that there is something wrong with H. N. Warren's statement because hydrogen is evolved at the cathode, and at the anode, a mixture of oxygen and nitrogen, quite free from fluorine, is given off. The anode liquor, however, contains something which liberates iodine from potassium iodide. Nitrogen fluoride is not formed by the action of fluorine on ammonium fluoride, nor by treating nitrogen chloride with silver fluoride; nor was H. Moissan able to make it by the action of fluorine on nitrogen in the cold, or by the action of the electric discharge on a mixture of nitrogen and fluorine.

About 1811, P. L. Dulong prepared *une nouvelle substance detonnante* by the action of chlorine gas on a soln. of an ammonium salt at 8°. This proved to be the violent explosive **nitrogen chloride,** NCl_3. He continued work on this compound after it had caused him the loss of three fingers and one eye. The preparation and handling of this compound require the greatest care. Every vessel employed must be washed by alkali-lye in order to free it from grease; even grease from the fingers may cause an explosion. The substance is very liable to spontaneous explosion, and thick gloves, and a face shield are indispensable. This question has been discussed by V. Meyer, and L. Gattermann. The substance may be formed in some

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reactions made with a totally different object—*e.g.* E. Dreyfuss mentioned its formation during the preparation of sulphamide; and F. Repiton, in some analytical work, obtained a violent explosion which he attributed to the unforeseen formation of this compound.

In preparing nitrogen by the action of chlorine upon aqueous ammonia, if the current of chlorine be continued after all the ammonia has been converted into ammonium chloride, the unmanageable explosive—nitrogen chloride—may be produced: $NH_4Cl+3Cl_2=4HCl+NCl_3$. Chlorine gas decomposes ammonia gas, or an aq. soln. of ammonia setting free nitrogen and hydrogen chloride, which unites with any unchanged ammonia, forming ammonium chloride: $8NH_3+3Cl_2=6NH_4Cl+N_2$. According to R. Porret and co-workers, a similar result obtains if the chlorine acts on a salt of ammonium and a weak acid; but if a salt of a strong acid be exposed to the chlorine gas—*e.g.* chloride, sulphate, phosphate, nitrate, or oxalate—the ammonia is to a certain extent protected from the action of the chlorine, and some of the explosive oil is formed, thus, $NH_4Cl+3Cl_2=4HCl+NCl_3$. This also occurs when chlorine in excess acts on aq. ammonia. W. A. Noyes and A. C. Lyon consider that the normal reaction between chlorine and ammonia should be symbolized: $12NH_3+6Cl_2 \rightarrow N_2+NCl_3+9NH_4Cl$, but only when the ammonia and chlorine are present in these proportions. If an excess of ammonia be present, it reacts with the nitrogen chloride giving free nitrogen: $NCl_3+4NH_3 \rightarrow 3NH_4Cl+N_2$, and ammonium hypochlorite: $NCl_3+2NH_3+3H_2O \rightleftharpoons 3NH_4OCl$; on the other hand, if a relatively small proportion of ammonia be present, the ammonium chloride formed in the reaction absorbs nitrogen, and the volume of nitrogen evolved will be less than that indicated by the normal equation—one-sixth the volume of the chlorine. W. A. Noyes and A. B. Haw said that in preparing the trichloride by this process a considerable proportion always decomposes into chlorine and nitrogen, either directly or by interaction between the trichloride and ammonia. The ratio of the number of mols. of chlorine to the number of mols. of ammonia may be varied between wide limits without affecting appreciably the ratio between the number of mols. of ammonia and the number of mols. of ammonium chloride. This ratio is 4 to 3. The chlorine reacts primarily with the ammonia, but only to a trifling extent, or not at all, with the solid ammonium chloride which is formed. According to C. T. Dowell and W. C. Bray, the reaction between chlorine and ammonia in strongly acidic soln. is typified by $NH_4Cl+4Cl_2=NCl_3+4HCl$; in strongly basic soln., by $8NH_3+3Cl_2=N_2+6NH_4Cl$; and in the presence of hypochlorous acid, by $NH_3+HOCl=H_2O+NH_2Cl$. They consider that the equation given by W. A. Noyes and A. C. Lyon is the resultant of a series of consecutive reactions the first of which is the formation of chloroamide · $NH_3+Cl_2=HCl+NH_2Cl$. L. Gattermann said that the product of the action of chlorine on ammonium chloride is a mixture of different chlorinated ammonias, and the composition depends on the conditions of the experiment. If the washed product be treated with chlorine, nitrogen trichloride is produced. W. A. Noyes said that ammonium sulphate is better than the chloride for preparing nitrogen trichloride.

R. Porret and co-workers said that 32° or upwards is more favourable for the production of nitrogen chloride than ordinary temp.; and that below 0°, none is produced. The presence of ammonium sulphide, sulphur, or powdered charcoal prevents the formation of nitrogen chloride; and this compound is not formed if the chlorine be mixed with one-third its vol. of air or carbon dioxide, or with an equal vol. of hydrogen. They prepared it by inverting a jar of chlorine over a dish containing a soln. of ammonium chloride at 32°. The oil forms a film on the sides of the vessel, and over the liquid, and finally sinks to the bottom in the form of oily drops. G. S. Sérullas inverted a jar of chlorine over a dish containing a warm soln. of ammonium chloride, and added more soln. to the dish as the liquid rose in the jar. When the chlorine was all absorbed, the jar was cautiously removed so as to prevent the oil attaching itself to the surface, and forming a film which volatilizes rapidly in air. A continuous current of luke-warm water was then passed into the dish containing the oil until the runnings were free from chlorides. J. J. Berzelius made nitrogen chloride by passing chlorine into a jar filled with a soln. of ammonium chloride, and inverted over a dish containing the same soln.

A. J. Balard noted that nitrogen chloride is formed when hypochlorous acid is in contact with ammonium chloride or sulphate, or aq. ammonia. W. Hentschel prepared nitrogen chloride by mixing a 5 per cent. soln. of sodium hydroxide sat. with chlorine, and a 10 per cent. soln. of ammonium chloride. The oil so formed was dissolved in benzene, chloroform, or carbon disulphide. The reaction is symbolized: $2NH_4Cl+7NaOCl=6NaCl+NaNO_3+4H_2O+NCl_3$. An excess of the hypochlorite produces chlorine which is dissolved by the nitrogen chloride. He also made the chloride by the action of a soln. of bleaching powder on ammonium chloride. If the soln. be alkaline, nitrogen chloride is not formed. H. Rai recommended the following procedure:

About 10 c.c. of a freshly prepared, filtered, conc. soln. of bleaching powder in a large test-tube are cooled in ice to about 0°, and an equal vol. of cold, sat. ammonium chloride soln. is added. When the vigorous reaction has subsided, after ten minutes, the nitrogen chloride is exploded by the addition of turpentine. The chloride on the surface explodes instantly, that at the bottom more violently after some time, the interval between the two explosions depending on the height of the liquid column, the amount of turpentine added, the nature of the surface explosion, and the amount of nitrogen chloride present. All apparatus must be absolutely free from grease and direct sunlight should be entirely excluded.

E. Dreyfuss, H. Rai, G. Lunge and R. Schoch, C. F. Schönbein, J. Thiele, H. Ditz, and T. Salzer studied the action of bleaching powder on a soln. of ammonium chloride. J. Kolb represented the reaction: $2NH_3+3CaOCl_2=3CaCl_2+3H_2O+N_2$. W. A. Noyes said that the treatment of an ammonium salt with hypochlorous acid gives a trichloride pure and free from chloro-amines. Nitrogen trichloride may be separated from a soln., in which it is prepared, by a current of air, drying the air and vap. of trichloride by passing through conc. sulphuric acid, and condensing the trichloride in a U-tube surrounded by a freezing mixture. J. Guinchant obtained nitrogen chloride by the action of hypochlorites on urea. According to R. Böttger, and H. Kolbe, drops of nitrogen chloride are formed on the anode during the electrolysis of conc. soln. of ammonium chloride. H. Hofer used a soln. of ammonium chloride sat. at 35°, and warmed to 40° by a current of 10–12 amps. and 7–8 volts. F. Mareck obtained a brown deposit on the cathode during the electrolysis of a cold sat. soln. of ammonium chloride. The nature of the deposit was not established.

The composition of the explosive product was represented by H. Davy as NCl_4; R. Porret and co-workers, by $NHCl_3$; N. A. E. Millon, as NH_2Cl; by J. H. Gladstone, as N_2HCl_5; and by A. Bineau, H. St. C. Deville and P. Hautefeuille, L. Gattermann, W. Hentzschel, P. L. Dulong, and D. L. Chapman and L. Vodden, NCl_3. The great explosiveness of the compound is referred by L. H. Friedburg to the internal strain induced by the chlorine atoms. T. T. Selivanoff said that nitrogen chloride is an amidoanhydride of hypochlorous acid, because this acid and not hydrochloric acid is developed when nitrogen chloride is hydrolyzed by water; and this hypothesis also explains why the chloride is so easily reduced with the formation of ammonia and chlorine by the action of hydrochloric acid. W. A. Noyes found that when nitrogen trichloride is titrated with a soln. of arsenious acid, one mol of trichloride is eq. to 6 gram-atoms of available chlorine, indicating that the nitrogen is negative and the chlorine positive, and that it hydrolyzes as a reversible reaction: $N'''Cl_3^{\cdot\cdot\cdot}+3H^{\cdot}O''H^{\cdot}=N'''H_3^{\cdot\cdot\cdot}+3H^{\cdot}O''Cl^{\cdot}$. He inferred that in the reaction between ammonia and chlorine, when nitrogen trichloride is formed, some chlorine molecules may be split up into Cl' and $Cl^{\cdot}$; and some of the nitrogen atoms may be temporarily positive and others negative. Hence, two nitrogen trichlorides are conceivable; in one—*nitro-nitrogen trichloride*—the nitrogen would be positive and the chlorine negative, and in the other—*ammono-*

nitrogen trichloride, presumably ordinary nitrogen chloride—the nitrogen is negative and the chlorine positive. W. A. Noyes believed that evidence of the existence of the nitro-nitrogen trichloride was obtained by passing a mixture of nitrosyl chloride and phosphorus pentachloride through a heated porcelain tube. Attempts to prepare nitro-nitrogen trichloride or nitrogen trichloride by passing mixtures of nitrogen and chlorine through a flaming arc were entirely unsuccessful. Passing the same gases through a powerful ozonizer had the same result and no action at all occurred with Strutt's active nitrogen. The results, although negative, confirm the hypothesis that electrons are held jointly by two atoms rather than the view that electrons are transferred from one atom to another when atoms combine. H. Henstock discussed the electronic structure.

H. Davy said that nitrogen chloride is a yellow, thick, oily liquid whose sp. gr. is 1·653; R. Porret and co-workers gave 1·6. I. I. Saslavsky discussed the mol. vol. H. Davy said that nitrogen chloride does not freeze at —40°. R. Porret and co-workers found that the chloride evaporates rapidly in air and can be distilled below 71°. The heat of formation worked out by H. St. C. Deville and P. Hautefeuille is —38·478 Cals. per eq.; and with the detonation at constant vol., a temp. of 2128° is attained, and a press. of 5361 atm.; with the detonation in air, at 760 mm., the temp. is 1698°. J. Thomsen was not satisfied with the above determination of the heat of formation. W. A. Noyes and W. F. Tuley found the heat of formation of nitrogen trichloride, in soln. in carbon tetrachloride, from gaseous nitrogen and chlorine, to be —54·7 Cals. R. Porret and co-workers said that the oily liquid does not conduct electricity.

The oil has a pungent odour which makes the eyes smart; and its action on the lungs is less powerful than that of chlorine. The physiological action was examined by W. Hentzschel. Nitrogen chloride explodes with great violence in many circumstances. There is a bright flash, a loud report, and the containing vessel may be shattered to bits. L. Gattermann said that a flash of direct sunlight, or magnesium light, may produce the explosion. He observed no explosion when the chloride was heated to 90°, but at 95° a sudden and violent explosion occurs. The destructive force seems to be downwards; this subject has been discussed by H. N. Warren, V. Meyer, and R. Wagner. Mere contact with many substances causes an explosion. W. Hentzschel found that nitrogen chloride dissolved in various organic solvents is decomposed by light usually with the formation of chlorination products. With carbon tetrachloride the reaction is simple: $2NCl_3 \rightarrow N_2+3Cl_2$; and E. J. Bowen measured the rates of decomposition in terms of the light energy absorbed, and concluded that more than one mol. is decomposed per quantum of energy absorbed.

According to R. Porret and co-workers, nitrogen chloride can be evaporated in **hydrogen, oxygen,** or atm. **air** without decomposition. A. Jouglet said that the chloride explodes in contact with **ozone.** When kept under cold **water,** H. Davy and G. S. Sérullas found that nitrogen chloride is decomposed within 24 hrs. with the formation of nitrogen and chlorine gases, and nitric and hydrochloric acids. T. T. Selivanoff suggested that in aq. soln. nitrogen trichloride is hydrolyzed $NCl_3+3H_2O \rightleftharpoons NH_3+3HOCl$; and in confirmation, D. L. Chapman and L. Vodden found that conc. **hydrochloric acid** reacts with a conc. soln. of nitrogen trichloride in carbon tetrachloride, forming chlorine and ammonium chloride: $NCl_3+3H_2O \rightleftharpoons NH_3+3HOCl$; $HOCl+HCl \rightleftharpoons Cl_2+H_2O$; and $NH_3+HCl \rightleftharpoons NH_4Cl$. Assuming the electronic theory of valency, N. V. Sidgwick said that when nitrogen trichloride reacts with water producing hypochlorous acid, its unshared pair of electrons are offered to the hydrogen of the water producing $Cl.N(Cl_2)-H.O.H$, which then decomposes. H. Davy also found that conc. hydrochloric acid gradually converts the oil into ammonium chloride with the evolution of chlorine gas: $NCl_3+4HCl = NH_4Cl+3Cl_2$. W. A. Noyes said that the formation of ammonium chloride from nitrogen trichloride and dry hydrogen chloride is not a hydrolysis when it occurs in the absence of water, and probably it is not a hydrolysis in the presence of water.

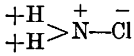
Rather does it consist primarily in the formation of *trichloroammonium chloride*, $(NCl^{\cdot}_3H)Cl'$, followed by the loss of an atom of positive chlorine with an atom of negative chlorine. The formation of nitrogen trichloride by the action of chlorine on a soln. of an ammonium salt appears to be the reverse of this reaction. T. T. Selivanoff found that dil. hydrochloric acid reacts with nitrogen chloride, forming hypochlorous acid, which is decomposed as fast as it is formed, and chlorine is evolved. C. T. Dowell and W. C. Bray showed that nitrogen trichloride, in carbon tetrachloride soln., reacts with a dil. soln. of **ammonium chloride,** and more rapidly with a conc. soln. $NH_4Cl+NCl_3=N_2+4HCl$. T. T. Selivanoff found that nitrogen trichloride decomposes in contact with **iodine,** and a dil. soln. of iodine yields iodic acid. C. T. Dowell and W. C. Bray found that a soln. of iodine reacts with nitrogen chloride in carbon tetrachloride soln. liberating nitrogen and forming iodine chloride —the addition of water results in the precipitation of iodic acid. If **potassium iodide** is used, 18 per cent. of the nitrogen is liberated as such, and the addition of sulphuric acid did not affect the result. According to N. A. E. Millon, an aq. soln. of **potassium bromide** forms nitrogen bromide or iodide, and potassium chloride. T. T. Selivanoff said that iodine is liberated from potassium iodide. G. S. Sérullas said that **sulphur** is without chemical action on nitrogen chloride, but is quietly dissolved. According to P. L. Dulong, sulphur decomposes nitrogen chloride, producing a substance which rapidly dissolves in water, forming a soln. of hydrochloric and sulphuric acids. G. S. Sérullas noted that contact with **selenium** produces an explosion; with an aq. soln. of **hydrogen sulphide,** milk of sulphur is deposited, a little nitrogen is evolved, and a soln. of ammonium chloride and hydrochloric acid formed. C. T. Dowell and W. C. Bray found that hydrogen sulphide reacts with nitrogen chloride in carbon tetrachloride soln., liberating 5·5 per cent. of the nitrogen and reducing the remainder to ammonia. R. Porret and co-workers found that contact with **hydrogen sulphide or persulphide** produces an explosion. N. A. E. Millon found that an aq. soln. of potassium sulphide produces a greenish-yellow powder which floats on the liquid. R. Porret and co-workers observed no action with **mercuric sulphide.** J. H. Gladstone showed that with **sulphurous acid,** nitrogen, ammonia, and hydrochloric acid are formed. C. T. Dowell and W. C. Bray found that of all the reducing agents tried, **sodium sulphite** was the only one which converted the whole of the nitrogen into ammonia when it acts on a carbon tetrachloride soln. of nitrogen trichloride: $3Na_2SO_3+NCl_3+3H_2O=3Na_2SO_4+2HCl+NH_4Cl$. H. Davy said that in contact with dil. **sulphuric acid,** nitrogen and oxygen are evolved. According to T. T. Selivanoff, dil. sulphuric acid forms a soln. containing hypochlorous acid, and the reaction is reversible. The iodide dissolves in **sulphur chloride.** R. Porret vaporized the chloride in **nitrogen** without any perceptible change. With conc. aq. **ammonia,** an explosion occurs, but H. Davy found that with a dil. soln., nitrogen is evolved and nitric acid formed. S. M. Tanatar obtained hydrazoic acid by the action of nitrogen chloride on **hydrazine.** C. T. Dowell and W. C. Bray found that with a carbon tetrachloride soln. of nitrogen chloride, both hydrazine and **hydroxylamine** give off nitrogen. R. Porret observed an explosion occurs when nitrogen chloride is brought in contact with **nitric oxide**; and H. Davy noted that with conc. **nitric acid,** nitrogen gas is evolved. G. S. Sérullas found that with a soln. of **silver nitrate,** nitrogen, nitric acid, and silver chloride are formed. G. S. Sérullas observed that contact with **phosphorus** causes nitrogen chloride to explode, and R. Porret and co-workers noted that soln. of phosphorus in carbon disulphide, **phosphine,** and **calcium phosphide** produce rather less violent explosions, and the decomposition by a soln. of phosphorus in ether is gradual. H. Davy said that nitrogen chloride is dissolved by **phosphorus trichloride**; and R. Porret and co-workers observed no reaction with dil. **phosphorous acid.** G. S. Sérullas found that nitrogen chloride explodes in contact with powdered **arsenic**; while R. Porret and co-workers said that arsenic is separated from **arsine** by the action of nitrogen chloride. G. S. Sérullas observed that with **arsenious acid,** ammonia is formed. C. T. Dowell and W. C. Bray found that a soln. of nitrogen chloride in carbon tetrachloride reacts with arsenious acid, liberating 7·7 per cent. of nitrogen, in the elemental form. Reducing the conc. of the soln. increases the yield of nitrogen, and with up to $0{\cdot}5N$-H_2SO_4, the yield of free nitrogen is augmented. The reduction of sodium arsenite soln. was also examined by W. Hentzschel, W. A. Noyes and A. C. Lyon, and D. L. Chapman and L. Vodden—*vide supra*. R. Porret could detect no reaction between native **antimony sulphide** and nitrogen chloride.

R. Porret and co-workers observed no reaction between **carbon** as charcoal on nitrogen chloride, and the chloride can be vaporized in an atm. of **ethylene** without undergoing chemical change. W. Hentzschel said that the chloride is dissolved by **benzene, chloroform, carbon tetrachloride,** and **carbon disulphide.** These soln. are sulphur-yellow, and refract light strongly; they are rapidly decomposed in light, but in diffuse daylight, or in darkness, they can be kept unchanged for weeks. The decomposition of an ethereal soln. is vigorous in sunlight, and some nitrogen is reduced to ammonia. The benzene soln. gives nitrogen and hexachloroethane when exposed to sunlight. The carbon tetrachloride soln. becomes yellow through the soln. of liberated chlorine, the chloroform soln. furnishes chlorine, hydrogen and ammonium chlorides, and hexachloroethane, but no carbon tetrachloride. The carbon disulphide soln. forms some sulphur chloride. R. Porret and co-workers said that the yellow soln. of nitrogen chloride in carbon disulphide does not explode with phosphorus or the fatty oils, but quietly sets fire to an excess of these substances; and, added G. S. Sérullas, the soln. is slowly decomposed under water into nitrogen, ammonia, hydrochloric acid, and sulphuric acid. The addition of phosphorus to the soln. causes a violent ebullition. N. A. E. Millon found that an explosion is produced when nitrogen chloride is brought in contact with **potassium cyanide**—solid or conc. soln.—a moderately dil. soln. producing potassium chloride and amidogen cyanide, while a dil. soln. disengages nitrogen gas only. Solid or an aq. soln. of **potassium thiocyanate** produces with nitrogen chloride an orange-yellow buttery mass, which dissolves in an excess of soln. R. Porret and co-workers observed no reaction with **potassium ferrocyanide.** T. T. Selivanoff found that nitrogen chloride is decomposed by a soln. of succinimide, forming chlorosuccinimide; the same product is obtained by the action of hypochlorous acid in place of nitrogen chloride. This and the other reactions of nitrogen chloride led T. T. Selivanoff to assume that nitrogen chloride is a derivation of hypochlorous acid—*vide infra*, nitrogen iodide. R. Porret and co-workers, C. T. Dowell and W. C. Bray found that a carbon tetrachloride soln. of nitrogen trichloride converts quinol into hexachloroquinol; and carbamide in acid soln. is not acted on, but in neutral soln. there is a slow evolution of nitrogen. They also observed that nitrogen chloride explodes in contact with various **organic substances.**

Thus, R. Porret and co-workers found that lead paint, margarates and oleates of manganese, copper, silver, and mercury; petroleum; amber oil, and amber; turpentine, camphorated olive oil; palm oil; train oil, olive oil; linseed oil; myrrh; and caoutchouc cause rapid decomposition. The decomposition is more or less gradual with margarates and oleates of barium, strontium, calcium, magnesium, potassium, aluminium, tin, and cobalt; ordinary resin, and ox-gall resin, and soln. of resin or shellac in alcohol. No decomposing action was observed with jet; shellac; frankincense; scammony; aloes; ethyl sulphate and nitrite; sugar; manna; gum; starch; indigo; gum kino; catechu; dried white-of-egg; benzoic acid; gum ammoniac; wax; spermaceti; stearine; butter; lard; or alcohol. Combination attended by a more or less partial decomposition occurs with asphalt, elaterite, copal, mastic, guaiacum, euphorbium, asafœtida, camphor, sulphuretted camphor, oil of musk, stearic and oleic acids, etc. W. Hentzschel found that aniline and nitrogen chloride in benzene soln. furnish trichloroaniline; methylaniline, trichloromethylaniline; and dimethylaniline, a chlorine derivative of tetraphenyl hydrazine. W. Strecker observed no reaction between benzene soln. of nitrogen chloride and magnesium ethyl iodide or magnesium phenyl bromide. G. H. Coleman and co-workers studied the addition products formed by the acetylene hydrocarbons with nitrogen trichloride dissolved in carbon tetrachloride.

P. L. Dulong, and H. Davy found that nitrogen chloride in contact with **copper** or **mercury** under water sets free nitrogen and forms a **metal** chloride; R. Porret and co-workers could detect no action on **tin** or **zinc.** G. S. Sérullas found that **lead, cobalt, copper, and silver oxides** decompose nitrogen chloride, forming chlorides and nitrates. A dil. soln. of **potassium hydroxide** forms the alkali chloride and nitrate with the evolution of nitrogen; R. Porret and co-workers found that an explosion occurs when nitrogen chloride is brought in contact with potassium hydroxide in the presence of water. C. T. Dowell and W. C. Bray found that when **sodium hydroxide** reacts with nitrogen trichloride there is a rapid evolution of nitrogen, and 7 per cent. of the nitrogen is recovered as ammonia; they also observed that **ferrous sulphate** reacts with nitrogen trichloride in carbon tetrachloride soln., forming nitrogen and ammonia.

The well-known bluish-violet colour reaction of aniline is or is not obtained with a hypochlorite according as ammonia is added after or before the hypochlorite and the aniline soln. are mixed. Moreover, whilst conc. soln. of ammonium hydroxide and sodium hypochlorite immediately evolve nitrogen when mixed, gas is evolved from dil. soln. only after some time. F. Raschig [2] inferred from these facts that there is formed an intermediate compound between ammonia and nitrogen. He showed that soln. containing equimolar proportions of ammonia and sodium hypochlorite react quantitatively: $NaOCl+NH_3=NH_2Cl+NaOH$; by adding, say, 50 c.c. of a soln. of 3·7 grms. of sodium hypochlorite—free from an excess of chlorine—to 100 c.c. of an aq. soln. containing 0·85 grm., the penetrating smell characteristic of monochloramide, NH_2Cl, appears. Some nitrogen is at the same time evolved owing to the decomposition of the monochloramide: $3NH_2Cl=N_2+NH_4Cl+2HCl$. No ammonium hypochlorite is formed. By distilling the liquid in vacuo at a low temp., *chloroamide*, or **chloroamine,** NH_2Cl, can be obtained as an unstable, pale yellow oil floating on the water in the receiver. There is much decomposition during the distillation. W. Marckwald and M. Wille said that the yellow liquid contains 10–12 per cent. of chloroamine. F. Raschig found that it can be distilled in vacuo in the presence of 50 per cent. zinc chloride without decomposition. For the action of soln. of hypochlorites on ammonia, *vide supra.* Chloroamine obtained as just described is a yellow mobile liquid. It attacks the eyes and nose like nitrogen chloride. When a conc. aq. soln. of chloroamine is kept at a low temp., it deposits yellow crystals of chlorine hydrate. W. Marckwald and M. Wille said that even at 0° the soln. soon commences to evolve nitrogen and to separate oily drops of nitrogen chloride. Its instability rapidly increases when it is preserved, decomposition being catalytically accelerated by the liberated acid. The course of the change is represented by the equations: $3NH_2Cl=NH_4Cl+2HCl+N_2$, $NH_2Cl+2HCl=NH_4Cl+Cl_2$, and $NH_2Cl+2Cl_2=NCl_3+2HCl$. Attempts to extract chloroform from its aq. soln. by means of benzene, chloroform, carbon tetrachloride, or ether had only limited success, the last-named solvent being the most suitable. The isolation of pure chloroamine has been rendered possible by the observations that its aq. soln. are greatly stabilized by the presence of very small amounts of ammonia. Even under those conditions, however, the concentration of the 10–12 per cent. soln. cannot be effected by distillation, since violent explosions invariably occur which are obviously due to the formation of nitrogen chloride. The vapours of the 10–12 per cent. soln. were therefore dried, and the unabsorbed portions condensed in a U-tube cooled in liquid air. For this purpose, calcium chloride and soda lime are unsuitable, since they influence the slight hydrolysis of chloroamine by water, $NH_2Cl+H_2O=NH_3+HClO$, in such a manner that the condensate consists of chlorine monoxide. Better results are obtained with anhydrous potassium carbonate. *Chloroamine* is thus obtained as a colourless, crystalline substance, m.p. $-60°$. It decomposes suddenly at about $-50°$ into nitrogen, chlorine, ammonium chloride, and nitrogen trichloride, and frequently explodes violently, so that its physical properties could not be further investigated. F. Raschig, and A. Stock found that chloroamine reacts with ammonia to form hydrazine and hydrogen chloride. According to F. Raschig, chloroamine reacts with *potassium iodide*, forming a brown soln., supposed to contain *iodamide*, NH_2I, which soon decomposes, forming ordinary nitrogen iodide, $NH_3.NI_3$. An acidified soln. reacts as symbolized: $2HI+NH_2Cl=NH_3+HCl+I_2$. Amidosulphonic acid is not formed by the action of *hydrosulphites* or *sulphurous acid*; rather is the sulphurous acid oxidized: $NH_2Cl+SO_2+2H_2O=NH_3+H_2SO_4+HCl$. The reaction with *potassium cyanide* is symbolized: $NH_2Cl+KCN+H_2O=NH_3+CNCl+KOH$. Chloroamine reacts with a soln. of *potassium hydroxide* almost quantitatively: $3KOH+3NH_2Cl=NH_3+N_2+3KCl+3H_2O$, and this the more rapidly the more conc. the soln. The alkali is always present in the mixture employed in making chloramide, so that there is a side reaction involving the production of ammonia and nitrogen—possibly from triimide, $N_3H_3=NH_3+N_2$. It was not found possible to realize the reaction, $NH_2Cl+NaOH=NaCl+H_2O+NH$, but the presence of traces of hydrazoic acid was established. The reaction between chloroamine and ammonia is similar to that with alkali-lye: $3NH_2Cl+2NH_3=N_2+3NH_4Cl$. At the same time, a small quantity of a reducing substance is formed. This was first observed by J. Thiele in his study of the action of ammonia on sodium hypochlorite. It is hydrazine formed by the consecutive reaction: $NH_2Cl+NH_3=N_2H_5Cl$. F. Raschig succeeded in hindering the first reaction and accelerating the second; by treating normal sodium hypochlorite soln., with 50 times the calculated quantity of ammonium hydroxide, in the presence of a little glue, there is produced 75–80 per cent. of the theoretical quantity of hydrazine (*q.v.*). In the presence of conc. alkali-lye, ammonia reacts in an analogous way, $NH_2Cl+NH_3+NaOH=N_2H_4+NaCl+H_2O$. This reaction also is favoured by the presence of formaldehyde, sugars, gum, or gelatin. According to W. Marckwald and M. Wille, the reaction with alkali-lye runs smoothly only when dil. soln. are employed; with conc. soln., the reaction takes place partly in accord with the scheme: $NH_4Cl+KOH=NH_3+KCl+H_2O$. F. Raschig obtained phenylhydrazine by the action of aniline in place of ammonia, and many substituted ammonias furnish substituted chloramides by treatment with hypochlorites. Thus, W. Meigen and W. Normann converted *p*-nitroaniline into *p*-nitrophenylmonochloramine. F. Raschig likewise treated *p*-amidophenol, *p*-phenylenediamine, *o*-toluidine, *p*-toluidine, β-naphthylamine, etc., with hypochlorites, and C. F. Cross and co-workers, proteids. H. Henstock gave for the electronic structure:



$$\begin{matrix}+\mathrm{H}\\+\mathrm{H}\end{matrix}\!>\overset{+}{\mathrm{N}}\!-\!\overset{-}{\mathrm{Cl}}$$

Nitrogen does not form a pentachloride. There are often curious changes in the degree of stable valency of the elements in a particular group. Nitrogen and arsenic do not form pentachlorides, while phosphorus and antimony do; nitric and arsenic acids readily give up oxygen, but phosphoric and antimonic acids are comparatively stable; the higher oxides of chlorine and iodine furnish a marked contrast with those of fluorine and bromine; and likewise the higher oxides of sulphur and tellurium, with those of oxygen and selenium.

According to N. A. E. Millon,[3] if an aq. soln. of potassium bromide is added drop by drop to nitrogen chloride covered by a layer of water, the yellow colour of the chloride slowly changes to red, which becomes deeper and deeper in tint. The dense black oil so obtained was considered to be a **nitrogen bromide.** It is very volatile, offensive-smelling oil which attacks the eyes very strongly. It explodes violently in contact with phosphorus or arsenic; under water, it is slowly decomposed, forming nitrogen, bromide, and ammonium bromide; and is decomposed by ammonia with the production of dense white fumes. H. W. B. Roozeboom obtained no trace of an explosive compound during the electrolysis of soln. of ammonium bromide.

The chocolate-coloured amorphous powder which was made by B. Courtois,[4] about 1813, by the action of an aq. soln. of ammonia on solid iodine, was thought by J. L. Gay Lussac, J. J. Colin, J. W. Mallet, and C. Stahlschmidt to be **nitrogen**

iodide, NI_3, analogous to nitrogen chloride, NCl_3. On account of the ease with which the product decomposes it is difficult to determine the composition; different results have been obtained by different methods of preparation. Nitrogen iodide is made by mixing iodine in various solvents—alcohol, chloroform, carbon disulphide, or aq. potassium iodide—with ammonia. R. Bunsen mixed cold sat. soln. of iodine and of ammonia in absolute alcohol, and washed the black product free from ammonium iodide by means of absolute alcohol: $2NH_3+3I_2=3HI+NH_3.NI_3$. G. S. Sérullas, J. H. Gladstone, and C. Stahlschmidt treated an alcoholic soln. of iodine with a conc. aq. soln. of ammonia, and washed with water. R. Bunsen, and G. S. Sérullas added ammonia to a dil. soln. of iodine in aqua regia and washed the precipitate rapidly with cold water: $2ICl+3NH_3=2NH_4Cl+NHI_2$, according to J. H. Gladstone; or $3NH_4OI=NH_3.NI_3+NH_3+3H_2O$, according to C. F. Schönbein. J. S. Stas purified iodine by first transforming it into nitrogen iodide, and then recovered the iodine. F. D. Chattaway and K. J. P. Orton mixed 300 c.c. of hydrochloric acid, sp. gr. 1·15, 28 c.c. of nitric acid, sp. gr. 1·41, and 100 grms. of iodine, at 40°, and then at 0°, added ammonia. Good crystals of nitrogen iodide can be obtained by adding ammonia to a soln. of potassium hypoiodite containing 0·02 mol per litre: $3NH_4OI=N_2H_3I_3+NH_4OH+2H_2O$. F. Raschig said that the precipitate obtained by the action of potassium iodide on a soln. of chloroamine, in the presence of ammonium chloride, is similar to that obtained by the action of iodine on aq. ammonia.

Nitrogen iodide does not appear to be formed by the direct substitution of iodine for hydrogen in ammonia, but the iodine reacts with ammonium hydroxide as it does with other alkalies, forming ammonium iodide; and T. T. Selivanoff considered that nitrogen iodide is most probably formed by the action of ammonia on hypoiodous acid which, along with ammonium iodide, is the first product of the reaction between ammonia and iodine: $NH_3+H_2O+I_2=NH_4I+HOI$, for the addition of a dil. soln. of iodine to ammonia gives a clear liquid containing hypoiodous acid; if more iodine is added, nitrogen iodide is precipitated and the clear liquor contains less of that acid than before. On the other hand, nitrogen iodide is soluble in a large amount of ammonia, forming hypoiodous acid so that the reactions $2NH_3+3HOI\rightleftharpoons NH_3.NI_3+3H_2O$, $NH_3+2HOI\rightleftharpoons NHI_2+2H_2O$, or $NH_3+3HOI\rightleftharpoons NI_3+3H_2O$, are reversible. It is claimed that this interpretation is supported by the fact that when a dil. soln. of iodine is added to ammonia, the liquid remains clear and contains hypoiodous acid. When a further quantity of iodine is added, iodide of nitrogen is precipitated, and the clear liquid then contains less hypoiodous acid than before. On the other hand, nitrogen iodide is soluble in a large amount of ammonia, yielding a soln. which contains hypoiodous acid, so that the three equations given above are reversible. It is to this formation of hypoiodous acid that many of the characteristic reactions of iodide of nitrogen must be referred, such as the liberation of oxygen from hydrogen peroxide, the formation of chloride of iodine by the action of hydrochloric acid, and the production of iodine derivatives from phenol. The accuracy of this view is further confirmed by the action of potassium iodide soln. and of dil. acids on iodide of nitrogen. Potassium iodide dissolves all the iodides of nitrogen more or less readily, and the soln. formed contains ammonia, iodine, and caustic potash, the reaction being represented by the following equations: $NHI_2+2H_2O=NH_3+2HOI$; and $2HOI+2KI=2I_2+2KOH$. Dil. acids, on the other hand, convert iodide of nitrogen into iodine and iodic acid, both of which are formed from hypoiodous acid according to the equation $5HOI=2I_2+HIO_3+2H_2O$. The change is usually accompanied by a certain amount of decomposition into iodine and nitrogen, but this can be wholly avoided if (1) a small amount of acid be employed, (2) sufficient water be present to dissolve the whole of the iodine formed, and (3) the iodide of nitrogen be in the form of a very fine powder. T. T. Selivanoff therefore proposed to call $NH_3:NI_3$, *sesquiiodylamine;* NHI_2, *diiodylamine;* and NI_3, *triiodylamine.* This view of the formation of nitrogen iodide is virtually that suggested by C. F. Schönbein, and is confirmed by the formation of this compound when ammonia is added to an alkaline soln. of potassium hypoiodite : $KIO+NH_4OH=NH_4OI+KOH$, and the ammonium hypoiodite thus formed decomposes into nitrogen iodide. L. Playfair made nitrogen iodide by the action of bleaching powder on a soln. of ammonium chloride, a reaction which J. H. Gladstone represented by $Ca(OCl)_2+2NH_4I=NH_4I_2+CaCl_2+2H_2O+NH_3$. J. J. André treated iodine trichloride, or a hydrochloric acid soln. of iodic acid with ammonia—J. H. Gladstone could not verify this method, but F. Raschig showed iodic acid and conc. hydrochloric acid form chlorine, and then iodine chloride, that which, when treated with ammonia, furnishes nitrogen iodide ; with dil. soln. the temp. should be raised. G. S. Sérullas obtained nitrogen iodide by treating a mixture of ammonium iodate, ammonium iodide, and hydrochloric acid with potassium hydroxide. J. Szuhay added an excess of aq. ammonia to a conc. soln. of iodine in one of potassium iodide. He represented the reaction by $3NH_3+2I_2=2NH_4I+NHI_2$. L. Dobbin and D. O. Masson found nitrogen iodide is formed in the decomposition of tetramethylammonium dichloroiodide, $(CH_3)_4NICl_2$; and C. Rice, in the action of alcohol and iodine on white precipitate —in this case, the presence of carbolic acid inhibits the reaction.

The composition and constitution of the so-called nitrogen iodide is uncertain. It will be observed that the equations for these various reactions depend on what view is taken of the composition of the final product. A. Bineau, F. Raschig, J. Szuhay, T. T. Selivanoff, and J. H. Gladstone represented its composition by NHI_2 ; N. A. E. Millon, and R. F. Marchand, gave NH_2I ; A. Guyard, $N_5H_5I_{10}$ and $N_8H_9I_{15}$; R.Bunsen obtained $NH_3.NI_3$ for the composition of the product formed in alcoholic soln., free from water ; and with iodine chloride and ammonia in aq. soln., $NH_3.4NI_3$. F. Raschig said that the first precipitate formed has the composition $NH_3.NI_3$, and with the washing it passes to explosive NHI_2, and then to NI_3. J. W. Mallet obtained $NI_3 : NI_3$; $NI_3 : NHI_2$; $NI_3 : NH_2I$; and $NHI_2 : NHI_2$. According to F. D. Chattaway and co-workers, the product of the different reactions is virtually the same if precautions be taken to remove free iodine and ammonia, and to prevent partial decomposition. When alcoholic soln. are used, the yield is reduced because of a secondary reaction between nitrogen iodide and alcohol giving iodoform, which contaminates the products. O. Ruff said that the formula is either $H_3N : NI_3$ or $I_3N : NI$; and it is generally agreed that in the so-called nitrogen iodide two nitrogen atoms are linked together to form either $H_3N : NI_3$, or $HI_2N : NHI_2$. The **nitrogen amminotriiodide** hypothesis is considered the more likely by F. D. Chattaway and co-workers, and others because nitrogen iodide which has stood under water for some time is very liable to explode, and analysis shows that an unstable nitrogen iodide, NI_3, is probably formed, but, if such a compound does exist, it is stable only in the presence of a large excess of iodine, and it has not been isolated. The term "nitrogen iodide" employed in describing the preparation and properties, refers probably to nitrogen amminotriiodide, $H_3N : NI_3$, when the nitrogen atoms are quinquevalent.

Nitrogen iodide as usually obtained by the different methods is a very dark brown or black powder. F. D. Chattaway and K. J. P. Orton obtained it in acicular crystals which were copper-red in reflected light, and red in transmitted light. The crystals are therefore dichroïc ; and probably belong to the rhombic system. The sp. gr. is 3·5. Although moist nitrogen iodide can be handled without danger of explosion, the dry compound is very explosive. Explosions are said to have been produced as a result of the shock of a falling dust-particle, and by a fly walking over the dry powder. N. A. E. Millon said that the iodide explodes when merely dried in air, and this the more readily, the higher the temp. The slightest movement, the least elevation of temp., or the addition of sulphuric or any other strong acid, whereby heat is probably developed, causes it to explode. When *under* water, the iodide does not usually explode unless strongly rubbed. Contact with oils and other fatty bodies does not usually cause it to explode. The explosion, said

N. A. E. Millon, is attended by a violet light, visible in the dark; the nitrogen is set free as a gas, and the iodine as a very fine powder. The white vapour formed during the explosion is probably ammonium iodide. R. F. Marchand also observed that traces of ammonium iodide are formed during the explosion; and R. Bunsen said that the first action is $NH_3+NI_3=N_2+3HI$, followed by the decomposition of the hydrogen iodide into its elements, while a little reacts with ammonia, forming ammonium iodide. P. Champion and H. Pellet showed that the explosion of nitrogen iodide at a distance can produce a second sympathetic explosion at some distance away by mechanical vibrations. The lowest number of vibrations are about 30 per second. Vibrations which give a deep sound have no effect, but shriller sounds readily explode the iodide. Heat unless accompanied by mechanical vibrations of the proper kind does not produce an explosion of the iodide.

Iodide of nitrogen was placed at the focus of a parabolic mirror, and at the focus of a second similar mirror, nitroglycerol, fulminate of mercury, and gunpowder were exploded. The quantity of nitroglycerol necessary to cause the explosion of the iodide of nitrogen in the other focus was determined; and it was found that as much powder was required as would produce ten times the heat given out in the burning of the required quantity of nitroglycerol. The mirrors were afterwards covered with lamp-black, and then even this large quantity of powder would not cause the iodide of nitrogen to explode, On the other hand, the lamp-black covering did not in the least prevent the nitroglycerol in one focus from exploding the iodide of nitrogen in the other.

J. Egert showed that the inter-molecular decomposition of nitrogen iodide takes place according to the equation $8NH_3NI_3=5N_2+6NH_4I+9I_2$, whether the decomposition takes place in the dark or in the light or is occasioned by detonation. Nitrogen iodide is not sensitive to shock, and many effects which were previously attributed to detonation are due to secondary mechanical effects. The sensitiveness of nitrogen iodide is not materially changed by lowering the temp. to —190°. Gradual isothermal increase of press. to 5000 atm. brings about a decomposition in 70 per cent. of the samples of nitrogen iodide. J. W. Mallet, and A. Guyard found that nitrogen iodide is decomposed by exposure to **light**, forming nitrogen, ammonium iodide and iodate; under water this decomposition usually proceeds quietly, but may end with an explosion; in ammonia the reaction proceeds quietly to the end. F. D. Chattaway and K. J. P. Orton found that the products with dry nitrogen iodide are nitrogen, iodine, and ammonium iodide; similar products are obtained when the iodide is decomposed by percussion or heat. A. Guyard found that the rapidity of the decomposition is proportional to the intensity of the light; and he added that heat rays are without action; the yellow rays are most active, the violet rays least active; but F. D. Chattaway and K. J. P. Orton said that the red rays are the most active, and that with decreasing wave-length the time required for the first appearance of gas bubbles increases; there is a second maximum with the blue rays. H. N. Warren found that nitrogen iodide instantly explodes, when exposed to the magnesium-light, while a few minutes' exposure is required with the limelight. According to F. D. Chattaway and K. J. P. Orton, nitrogen iodide in ammonia is decomposed by sunlight or artificial light: $NH_3.NI_3=N_2+3HI$; with the simultaneous reaction $NH_3.NI+3H_2O=2NH_3+3HOI$; and $NH_3+HOI=NH_4OI$; while the hypoiodite then decomposes into ammonium iodide and iodate. Nitrogen iodide suspended in **water** behaves in a similar way, but under water, there is also the additional reaction: $NH_3.NI_3+5HI=2NH_4I+3I_2$. The ammonium iodate produced represents 2 to 4 per cent. of the original nitrogen iodide. The production of the hypoiodite is a hydrolytic process and proceeds in light or in darkness, but the formation of nitrogen and hydrogen iodide only occurs in light. According to G. S. Sérullas, N. A. E. Millon, and J. S. Stas, nitrogen iodide gradually dissolves under cold water, forming in 4–6 weeks ammonium iodide and iodate; and some free iodine. If the temp. be raised, the dissolution proceeds more rapidly; at 70°, the reaction is turbulent; and in boiling water, an explosion occurs. G. S. Sérullas, and

N. A. E. Millon said the aq. soln. is neutral; J. H. Gladstone, acid. A. Guyard said that the nearer the composition of the iodide approaches NHI_2, the less is it changed by washing with water; and F. D. Chattaway and K. J. P. Orton found that nitrogen iodide is hydrolyzed by water and alkaline soln.—ammonia and an hypoiodite are formed: $N_2H_3I_3+3KOH=2NH_3+3KOI$; or $N_2H_3I_3+3H_2O=2NH_3+3HOI$. The hypoiodite breaks down more or less rapidly into iodide and iodate: $3KOI=2KI+KIO_3$; or $3HOI=2HI+HIO_3$. In the latter case, the products of the reaction interact, forming iodine: $5HI+HIO_3=3I_2+3H_2O$. In darkness, the hydrolytic action of water with the production of iodine, and ammonium iodide and hypoiodite explains how with washing, the nitrogen content of ammonium iodide is reduced; until finally nothing but iodine remains. F. Raschig said that the original precipitate, $NH_3.NI_3$, reacts with sodium hydroxide as symbolized: $NH_3.NI_3+4NaOH=NH_3+3NaI+2H_2O+NaNO_2$; and $NH_3.NI_3+3NaOH=N_2+3NaI+3H_2O$. According to C. F. Schönbein, an aq. soln. of **hydrogen dioxide** decomposes nitrogen iodide turbulently with the evolution of oxygen and a little nitrogen, and the formation of a brown soln. of iodine, hydriodic acid, ammonium iodide, and a trace of iodic acid. F. D. Chattaway found that in alkaline soln., hydrogen dioxide forms ammonia, alkali iodide, a trace of iodate, oxygen, and a little nitrogen.

J. H. Gladstone found that **chlorine** slowly decomposes nitrogen iodide; a similar result was obtained with **bromine** water. P. Champion and H. Pellet said that the iodide explodes by contact with chlorine or bromine. According to G. S. Sérullas, and N. A. E. Millon, when dil. **hydrochloric acid** is gradually added to nitrogen iodide, under water, the iodide dissolves completely with the evolution of gas, and the soln. contains ammonium chloride, iodide, and iodate. Nitrogen iodide is again precipitated from the soln. if alkali-lye be added because the ammonia set free by the alkali reacts with the two salts of iodine present. J. H. Gladstone represented the reaction, $NHI_2+3HCl=NH_4Cl+2ICl$; R. Bunsen, $NH_3.NI_3+5HCl=2NH_4Cl+3ICl$; and C. Stahlschmidt, $NI_3+4HCl=NH_4Cl+3ICl$. F. D. Chattaway found that in contact with dil. **acids,** nitrogen iodide is hydrolyzed $N_2H_3I_3+3H_2O=2NH_3+3HOI$. The ammonia combines with the acid, and the hypoiodite breaks down in a way which depends upon the nature of the acid used: with **phosphoric, acetic, boric, or sulphuric acid,** the reaction is of the type $3HOI=2HI+HIO_3$, followed by $5HI+HIO_3=3I_2+3H_2O$; with acids which can react with hypoiodous acid, other changes occur, for instance, with **hydriodic acid and hydrochloric acids,** $HOI+HI=I_2+H_2O$; $HOI+HCl=ICl+H_2O$, and with **hydrocyanic acid,** $HOI+HCy=ICy+H_2O$. With conc. acids, a violent explosion results. F. D. Chattaway and K. J. P. Orton also examined the action of **lead and silver iodides.** A. Guyard said that **potassium iodide** and nitrogen iodide, in darkness form potassium polyiodide free from ammonia; and **cupric iodide** forms cuprous iodide, and ammonium polyiodide. When an ammoniacal soln. of a copper salt is mixed with potassium diiodide, a brilliant, crystalline, garnet-coloured precipitate of **copper nitrogen iodide,** $CuI_2,2NH_2I$, is gradually deposited. When dried, this compound is very stable, but it is entirely decomposed by water, with formation of ammonium diiodide, and a bronze-coloured cupric oxyiodide, CuO_2I, which is decomposed by heat into black cupric oxide, iodine, and oxygen. The double copper nitrogen iodide is decomposed by aq. ammonia, with formation of an ammoniacal soln. of cupric iodide and a residue of an explosive nitrogen iodide free from copper. When the double iodide is heated, iodine and the products of the decomposition of nitrogen iodide are given off, and a residue of perfectly pure cuprous iodide is left. When distilled, the double iodide yields cuprous iodide, and brown, violet, and ammoniacal vapours. The brown vapours condense to a black product, decomposed by water with formation of a black crystalline nitrogen iodide, which resembles iodine in appearance, but which differs from all the other nitrogen iodides by dissolving with effervescence in a soln. of potash or soda, nitrogen or hydrogen being given off, and a considerable quantity of ammonia formed.

According to G. S. Sérullas, A. Bineau, J. H. Gladstone, F. D. Chattaway, and C. Stahlschmidt, nitrogen iodide is almost instantly decomposed by **hydrogen sulphide** with the separation of sulphur, but with no evolution of gas; the resulting soln. contains ammonium iodide mixed with a slight excess of hydriodic acid. J. H. Gladstone, and F. D. Chattaway found that an aq. soln. of **sulphur dioxide** decomposes nitrogen iodide into hydriodic acid. The former gave for the equation $NHI_2+2SO_2+4H_2O=NH_3+2HI+2H_2SO_4$. A. Bineau represented the reducing action of sulphurous acid, $NHI_2+2H_2=NH_4I+HI$. F. Raschig represented the reaction with **sodium sulphite**: $NH_3.NI_3+3Na_2SO_3+3H_2O=2NH_3+3HI+3Na_2SO_4$. A. Guyard found that **sodium thiosulphate** furnishes sodium iodide, ammonia, and ammonium sulphate, and F. D. Chattaway represented the reaction: $N_2H_3I_3+3Na_2S_2O_3+3H_2O=2NH_4I+HI+3Na_2SO_4+3S$, and some sodium tetrathionate is formed. According to F. D. Chattaway and H. P. Stevens, **reducing agents** rapidly decompose nitrogen iodide, the reducing agent is oxidized, and hydriodic acid and ammonia are formed. The contained iodine behaves like the contained chlorine in hypochlorites. If R represents the reducing agent, $N_2H_3I_3+3H_2O+R=(RO_3)+2NH_4I+HI$. One mol. of hydrogen iodide is produced for every mol of **sodium sulphite, sulphurous acid, stannous chloride** or **hydrogen sulphide** oxidized, and two mols of hydrogen iodide for every mol of **arsenic or antimony trioxide** oxidized. A. Bineau found that arsenic trioxide in aq. soln. slowly dissolves nitrogen iodide without the evolution of gas: $NHI_2+2H_2O+As_2O_3=NH_4I+HI+As_2O_5$.

W. Biltz discussed the stabilization of nitrogen triiodide by **ammonia.** C. Stahlschmidt showed that nitrogen iodide is decomposed by **methyl iodide**; H. von Gilm, by **ethylamine**; and O. Silberrad, by **zinc ethyl.** A. Guyard showed that a soln. of **potassium cyanide** dissolves nitrogen iodide with the evolution of nitrogen. F. Raschig represented the reaction: $NI_3+3KCy+3H_2O=NH_3+3KOH+3ICy$. The reaction was also studied by N. A. E. Millon, and F. D. Chattaway. A. Bineau found that **zinc** is dissolved when in contact with water and nitrogen iodide: $NHI_2+2Zn+H_2O=NH_3+ZnO+ZnI_2$. F. D. Chattaway examined the action of **arsenic** and **antimony** on nitrogen iodide. J. Szuhay observed that moist **silver oxide** or an ammoniacal soln. of **silver nitrate** gives a black, insoluble, explosive silver iodoamide, $AgNI_2$. If iodine chloride be added to an ammoniacal soln. of a silver salt, O. Silberrad found that silver iodoamide, $AgNH_2.NI_3$, is formed. G. S. Sérullas showed that a soln. of **potassium or calcium hydroxide** slowly dissolves nitrogen iodide suspended in water, forming ammonia, potassuim iodide, and iodate, and a trace of nitrogen: $3NHI_2+6KOH=2KIO_3+4KI+3NH_3$. More nitrogen is given off with a conc. soln. of potash-lye owing to the rise of temp. which occurs at the same time. F. D. Chattaway and K. J. P. Orton say that the main reaction is an hydrolysis: $N_2H_3I_3+3KOH=2NH_3+3KOI$, followed by $3KOI=2KI+KIO_3$—a part of the nitrogen iodide is simultaneously transformed with nitrogen and hydriodic acid. With soln. of potassium or sodium carbonate, ammonia, and alkali iodide and hypoiodite are simultaneously formed. C. Hugot represented the action of **sodammonium:** $3NaNH_3+NH_3.NI_3=4NH_3+3NaI+N$.

N. A. E. Millon,[5] and A. Bineau found that dry iodine absorbs dry ammonia such that, according to the former, 100 grms. of iodine takes up 8·3 grms. of ammonia at 10°; 9 grms. at 0°; 9·4 grms. at −18°. At −0°, and over, the rise of temp. accompanying the absorption leads to the evolution of a little nitrogen. J. J. Colin, and A. Bineau also said that a combination of ammonia and iodine is obtained by gently warming a mixture of iodine and ammonium sesquicarbonate. According to N. A. E. Millon, the reddish-brown liquid is **iodomonammine,** NH_3I; and, according to A. Bineau, **iodohemitriammine,** $I_2(NH_3)_3$. F. Raschig found that at 20° the amount of ammonia taken up by iodine corresponds with A. Bineau's formula: at 80°, with N. A. E. Millon's; at 0°, with **iododiammine,** $I(NH_3)_2$; and at −10°, with **iodohemipentammine,** $I_2(NH_3)_5$. According to J. L. Gay Lussac, the iodoammine is decomposed when heated, and ammonia is evolved. G. Landgrebe noted that if an excess of ammonia be employed the product is as limpid as water, but on exposure to air, the liquid thickens. Water was found by J. L. Gay Lussac to decompose the iodammine into aq. ammonia iodide, and nitrogen iodide; a current of hydrogen chloride was found by N. A. E. Millon, to convert it into nitrogen, ammonium chloride, ammonium iodate, and free ammonia. F. Raschig said that iodammine dissolves readily in alcohol without suffering any change. The work of C. Hugot, and O. Ruff makes it doubtful if any of the iodammines are chemical individuals—*vide supra*, nitrogen iodide.

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§ 47. Nitrosyl Halides

G. Gore[1] found that when a mixture of sodium fluoride and nitrate, and sulphuric acid is distilled, a colourless liquid which fumes less than hydrofluoric acid is formed. It does not attack platinum or paraffin; and it vulcanizes caoutchouc rapidly. O. Ruff and K. Stäuber could not obtain any definite compound in this way, but by treating silver fluoride with nitrosyl chloride, at 200°–250°, and fractionating the cooled product, they obtained **nitrosyl fluoride,** NOF, as a colourless solid which melts at about —134°, forming liquid which boils at —56°. O. Ruff and co-workers also obtained it by heating the complex $SbF_5.NOF$, or $AsF_5.NOF$, in a platinum tube with powdered potassium fluoride for 4–5 hrs. at 320°. A complex with the arsenic or antimony fluoride is set free. The gas is colourless, attacks dry glass slowly, and moist gas rapidly. The vap. density 1·683–1·699 at about 23° and 760 mm. is 1·683, which is very near that required for NOF. The gas, in many respects, behaves like fluorine and nitroxyl fluoride. With water, it forms a blue soln. which decomposes, forming nitric oxide and nitric acid; and it does not react with iodine in the cold or when heated; it does not react with sulphur—cold or hot; similar remarks apply to carbon. The reaction between nitrosyl fluoride and silicon, boron, or red phosphorus in the cold is accompanied by incandescence; arsenic and antimony also react in the cold with the development of much heat; tin, when warmed in the gas, gives a white vapour; sodium under similar conditions forms sodium fluoride with incandescence; copper, aluminium, lead, and bismuth react feebly with the gas; many organic substances—starch, caoutchouc, etc.—are attacked with the formation of hydrogen fluoride. In reactions with the metals, nitric oxide is formed; and in double decompositions, nitrogen peroxide is produced. W. Lange prepared **nitrosyl fluosulphonate,** $NO.SO_3F$, mixed with a little nitrosylsulphuric acid, by passing nitrogen trioxide, dried by calcium nitrate and phosphorus pentoxide, into ice-cold fluosulphonic acid. The colourless crystals are very hygroscopic. The compound is decomposed by water, and alkali-lye. It softens at 118°, and melts at 140°.

According to J. L. Gay Lussac,[2] two vols. of nitric oxide unites with one vol. of chlorine to form a gas which, at —15° to —20° condenses to form a mixture of **nitrosyl chloride,** NOCl, and nitrosyldichloride, $N_2O_2Cl_4$, or $NOCl_2$. E. Briner and Z. Pylkoff said that the product contains chlorine in soln., and N. Boubnoff amd P. A. Guye found that the excess of nitric oxide can be removed by distillation at —150° to —160°; and the excess of chlorine by fractional distillation at —80°—the chlorine is retained at —150°. E. Wourtzel, and E. Briner and Z. Pylkoff purified nitrosyl chloride by crystallization and fractional distillation in the presence of phosphoric oxide. L. Francesconi and G. Bresciani obtained a good yield of nitrosyl chloride by passing the dried mixture of nitric oxide and chlorine over dried animal charcoal at 40°–50°. E. Briner and Z. Pylkoff said the animal charcoal is necessary as a catalyst, for its presence does not affect the yield. E. Schering patented the use of activated charcoal as a catalyst, claiming that the nitrosyl chloride is formed in better yields; and more rapidly than when a mixture of the nitric oxide and chlorine is led over ordinary porous charcoal. A. Kiss found that the reaction is not much accelerated by one to two per cent. of nitrogen peroxide, but 10 per cent. considerably hastens the reaction. This catalysis involves the rapid reaction: $2NO_2+Cl_2=2NO_2Cl$; and the slow reaction of the second order:

$NO_2Cl+NO=NOCl+NO_2$. These reactions are independent of the surface of the containing vessel, and are not affected by light. M. Trautz and W. Gerwig measured the velocity of absorption of nitric oxide by liquid chlorine, and they calculated velocity constants of the reactions involved, which are (1) $2NO+Cl_2 \rightarrow 2NOCl$, for which the velocity constant k is of the order 10^7, (2) $NO+Cl_2 \rightarrow NOCl_2$, and (3) $NOCl_2+NO \rightarrow 2NOCl$, for which k (mols. per c.c. and seconds) is of the order 10^2. Within the limits of error of the method, the velocities of the pseudo-bimolecular reaction (1) and of the termolecular decomposition of $NOCl_2$ (2) are the same if the reaction takes place in the gaseous state or in liquid nitrosyl chloride as solvent. F. A. Henglein observed no difference in the rate of formation of nitrosyl chloride when the system is exposed to a magnetic field of 20,000 gausses.

E. Davy obtained impure nitrosyl chloride—or as he called it *chloronitrous acid*—as an orange-yellow gas when nitric acid acts on potassium or sodium chloride; J. L. Gay Lussac showed that the product also contains hydrochloric acid; and that the proportions of nitrosyl chloride and hydrochloric acid so formed depends on the conc. of the acid, and the temp. W. C. Williams obtained nitrosyl chloride by the action of chlorine on nitrogen peroxide; R. Müller, by passing hydrogen chloride through nitrogen peroxide at −22°; $NO_2+2HCl=NOCl+H_2O+Cl$. The liquid becomes red, and some chlorine is evolved. When fractionated, nitrosyl chloride passes off at −10°; nitroxyl chloride at 10°–12°; and there remains nitric acid mixed with some nitrogen peroxide. E. Briner and Z. Pylkoff found the product is contaminated with chlorine and nitrogen oxides; and likewise also with that prepared by the action of hydrogen chloride on liquid nitrogen trioxide: $N_2O_3+2HCl=2NOCl+H_2O$. E. Briner and A. Wroczynsky observed that nitroysl chloride is formed when a mixture of nitric oxide and hydrogen chloride is submitted to a press. of 300 atm. When nitric oxide is allowed to remain at high press. in a sealed tube, it is colourless at first, but after a day appears bluish-green. If the tube contains a large quantity of the gas, drops of a blue liquid appear. The reaction is supposed to be represented by $6NO=2N_2O_3+N_2$; the synthesis of nitrosyl chloride would then be explained by the action $N_2O_3+2HCl=2NOCl+H_2O$. No action occurs unless the nitric oxide is above a certain minimum press. When the press. in the tubes was gradually increased, the blue gaseous phase was first noticed at 28 atm. The rate of formation of nitrosyl chloride increases with the press. M. Trautz and H. Schlüter showed the empirical identity of the chemical conception—formation of an intermediate compound—and the physical conception—duration of molecular impacts—inter- and multi-molecular collisions. The reaction between nitric oxide and chlorine, which is purely termolecular within wide ranges of temperature and concentration, is shown to proceed in two stages in accordance with the impact duration law, thus: $NO+Cl_2=NOCl_2$ and $NOCl_2+NO=2NOCl$. The velocity constants for each stage of the reaction are in agreement with those deduced from the law of mass action, and the temp. coeff. agree with the requirements of the reaction velocity isochore. All reactions of an order higher than the second occurring in dil. systems of liquids or gases are considered to be superimposed reactions of the first or second order.

A. Lachmann prepared nitrosyl chloride by the action of hydrogen chloride on diphenylnitrosamine at 0°. A. C. Girard and J. A. Pabst, W. A. Tilden, R. H. Pickard and H. Hunter, and J. J. Sudborough and J. H. Millar made nitrosyl chloride by distilling a mixture of potassium or sodium chloride and nitrosyl sulphonic acid; E. Briner and Z. Pylkoff said that this mode of preparation gives a product with the least contamination. Nitrosyl chloride is the chief constituent of aqua regia (*q.v.*). According to E. Divers and T. Haga, if nitric acid and hydrogen chloride are allowed to react with an excess of stannous chloride hydroxylamine chloride is produced, but if insufficient stannous chloride is present nitrosyl chloride and nitrous oxide are formed. W. C. Williams obtained nitrosyl chloride by the action of nitric acid on an excess of phosphoryl chloride; A. Geuther, from hyponitrous acid and hydrogen chloride or phosphorus trichloride or pentachloride; and by the action of nitrous acid on phosphorus trichloride. A. Naquet made nitrosyl chloride by mixing molar proportions of potassium nitrate and phosphorus pentachloride in the cold, and separating the resulting phosphoryl and nitrosyl chlorides by fractionation; and V. Thomas prepared it by the action of nitric oxide on ferric chloride—*vide supra*, nitric oxide and chlorine. A. Pinkus and M. de Schulthess studied the ionization which occurs during the combination of chlorine with nitric oxide. The ionization is due to the emission of bipolar nuclei produced by the chemical reaction itself, and is not in any way influenced by any physical process. Generally, the ionization is very intense, but the number of charged particles received by the electrode is always very much less than the number of nitrosyl chloride mols. formed. This is explained, at least in part, by the recombination of the ions before they reach the electrode. The ionization is favoured by an excess of chlorine, the strongest effect being observed when 1 to 4 vols. of chlorine are mixed with one vol. of nitric oxide. The number of charges received by the electrode in a given time is independent of the press. of the reacting mixture. The ionization persists generally for a few minutes only, and its intensity decreases much more rapidly than the rate of formation of the nitrosyl chloride. The results generally indicate that the ionization is brought about by the reaction of at least one mol. of chlorine with one mol. of nitric oxide, and it occurs more rapidly than the reaction $2NO+Cl_2=2NOCl$.

Nitrosyl chloride was analyzed by R. Müller, E. Wourtzel, and P. A. Guye and G. Fluss; the results agree with the empirical formula NOCl. At ordinary temp., nitrosyl chloride is a gas which condenses, when cooled, to a yellowish-red liquid. E. Wourtzel found the vap. density is normal. R. Müller, and A. C. Girard and J. A. Pabst gave —5° for the b.p.; A. Baudrimont, —7·2°; W. A. Tilden, —8°; A. Geuther, 2°; and L. Francesconi and G. Bresciani, —5·6°. A. Geuther gave 1·4165 for the sp. gr. of the liquid at —12°, and A. Baudrimont, 1·3677 at 8°. E. Briner and Z. Pylkoff gave for the sp. gr., D, at different temp., θ,

	40°	24·9°	11·9°	0·5°	—8·6°	—26·7°	—47·6°	—56·8°
Sp. gr., D	1·221	1·285	1·319	1·346	1·367	1·406	1·478	1·552

They represented the results by $D=1{\cdot}349-0{\cdot}00242\theta$. E. Rabinowitsch gave 48·1 for the mol. vol. E. Briner and Z. Pylkoff found for the viscosity 0·00547 at —20°; 0·00567 at —25·2°; 0·00586 at —27°; 0·00604 at —29·5°; and 0·00642 at —33·3°. The surface tensions at —33°, —22°, and —5·5° were respectively 34·5, 32·7, and 30·3 dynes per centimetre; the specific cohesion, 0·0492, 0·0474, and 0·0456 mgrm. per millimetre respectively; and the surface energy, $\sigma(M/D)^{\frac{2}{3}}$, 441, 424, and 400 ergs respectively. F. de Block represented the surface tension at $\theta°$ by $\sigma=\sigma_0(\theta_c-\theta)^{0{\cdot}891}$, where θ_c represents the critical temp.—*vide supra*, nitrogen. A. Baudrimont gave 5 mm. for the capillary ascent at —6·8° in a tube 1·2 mm. bore. According to W. J. van Heteren, nitrosyl chloride freezes, forming blood-red crystals which melt at —65°; N. Boubnoff and P. A. Guye said —64·5°, Fig. 99. L. Francesconi and G. Bresciani found that nitrosyl chloride furnishes lemon-yellow crystals at the temp. of liquid air, and the crystals were said to melt at —60° to —61°. P. A. Guye and G. Fluss gave —61° for the b.p. and —5·6 for the m.p.; M. Trautz and W. Gerwig, —5·8° for the m.p., and 61·5° for the b.p. The critical temp. is 163°–164°. E. Briner and Z. Pylkoff gave 167° ±2°, and for the critical press., 92·4 atm. W. A. Tilden gave from 33 to 33·5 for the vap. density of 10°—hydrogen unity. The at. vol. of chlorine and nitrogen being uncertain, E. Briner and Z. Pylkoff showed that the mol. wt. of nitrosyl chloride cannot be estimated from density measurements alone, but the application of G. Longinescu's relation between the b.p. and density, and W. Ramsay and J. Shields' observations on the surface energy indicate that nitrosyl chloride is slightly polymerized. The last relation, of course, refers to the state of the molecules in the surface film, and not in the bulk of the liquid. W. A. Kistiakowsky's relation between the b.p. and surface tension; P. Dutoit and P. Mojoiu's relation between the b.p., surface tension, and vap. press.; P. Walden's relation between the b.p., surface tension, and critical temp.; and A. J. Batschinsky's relation between the viscosity and temp.—all indicate that the mol. of nitrosyl chloride is not polymerized. According to J. J. Sudborough and J. H. Millar, the vap. density at 700° is 32·65—hydrogen unity—which agrees with the formula NOCl; and at higher temp., the compound dissociates. The vap. density, *D* (hydrogen), and the percentage dissociation at different temp. are:

	784°	796°	815°	928°	968°	985°
	31·77	31·36	31·00	29·00	27·30	27·00
Dissociation	5·54	8·22	10·64	25·17	39·19	41·85 per cent.

They therefore said that nitrosyl chloride is a very stable compound, and is to be regarded as the chloride of nitrous acid, O=N—Cl. M. Trautz and co-workers showed that the dissociation of nitrosyl chloride can be detected at 250°. According to H. A. Taylor and R. R. Denslow, 3·54 per cent. is dissociated at 733°; 4·00 per cent. at 752°; 4·47 per cent. at 806°; and 5·64 per cent. at 1123°. The effect of increasing the surface is negligible, so that a purely gas reaction is involved. The energy of activation is 6000 Cals.; this corresponds to a wave-length of 4·769μ, but, so far as is known, this does not correspond to any band in the absorption spectrum. E. Briner and Z. Pylkoff gave for the vap. press. *p* mm.:

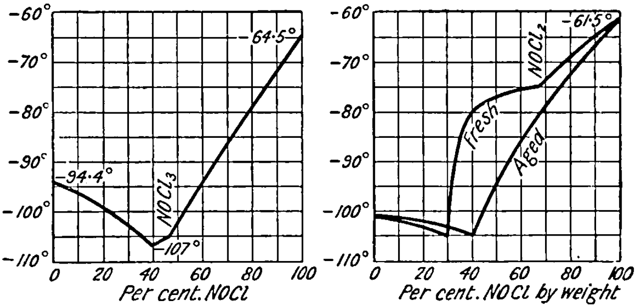
	−68·6°	−60°	−50°	−40°	−30°	−20°	−10°	0°	10°
p	55	130	210	280	360	470	660	890	1420

M. Trautz and W. Gerwig obtained different values and represented their results by log $p=-1332T^{-1}+7\cdot867$ mm. They gave 5·35 Cals. for the mol. heat of vaporization; while E. Briner and Z. Pylkoff gave $\lambda=5\cdot56$ Cals., or $\lambda/T=9\cdot5 \log T -0\cdot007T$. M. Trautz and C. F. Hinck calculated the heat of formation to be 18 Cals.; and G. N. Lewis and M. Randall, the free energy change, between 500° K. and 750° K., to be $-9100+14\cdot3T$.

J. E. Coates and A. Finney measured the rate of formation of nitrosyl chloride from eq. mixtures of nitric oxide and chlorine, by the decrease in press. The results agreed best with the assumption that the reaction is termolecular. The velocity constant is $4\cdot2\times10^{-6}$ at 0° when the press. is expressed in millimetres of mercury and time in minutes. A. Kiss gave $2\cdot62\times10^{-6}$ at 18°. The temp. coeff. is small, being about 1·23 per rise at 10°; M. Trautz gave 1·15. A. Kiss said that the termolecular reaction is accelerated by the presence of water vap., although water does not act as a catalyst in the reaction between nitric oxide and chlorine at 18°. The formation of nitrosyl chloride either directly or through the intermediate stage of nitrosyl bromide is not affected by light; the direct formation is stimulated by the catalytic effect of a rough surface. The reaction velocity is not affected by the presence of hydrogen chloride or carbon dioxide, and if light is excluded both hydrogen and carbon monoxide are without effect. The rate of formation of nitrosyl chloride between 0° and 78° is the same whether the mixture is illuminated or preserved in the dark. The decomposition of nitrosyl chloride under the influence of white light is strictly unimolecular. The temp. coeff. of the velocity constant over the range 0° to 78° is unity. D. Alexejeff calculated the dissociation constant to be log $K_c=-5\cdot01$ at 450° K.; $-3\cdot78$ at 503° K.; $-3\cdot08$ at 543° K.; and $-1\cdot90$ at 593° K. The reaction was studied by S. Dushman, and E. Moles; and the photochemical decomposition of nitrosyl chloride, by A. Kiss; and also by E. J. Bowen and J. F. Sharp who worked with light in the spectral range 4400 A. to 5200 A. They estimated that two quanta are absorbed per mol decomposed; and showed that the heat of the reaction $NOCl+45{,}000\text{ cals.}\rightarrow NO+Cl$ agrees with the assumption that the maximum wave-length capable of causing decomposition is 6270 A., which corresponds almost exactly with the point at which the absorption of nitrosyl chloride begins, but the absorption in red light is too weak to enable the decomposition to be studied.

Since the quantum of blue light is greater than the minimum quantum necessary for decomposition, it is probable that the decomposition is a true unimolecular process, $NOCl+h\nu=NO+Cl$, followed by spontaneous reactions re-forming nitrosyl chloride, possibly through the intermediate compound $NOCl_2$. For the meaning of $h\nu$, *vide* 1. 13, 15. The rate of reaction does not therefore follow the unimolecular equation, in contradiction to the assumption of A. Kiss. G. Magnanini found that the absorption spectrum of nitrosyl chloride has six bands in the orange and green parts of the spectrum.

H. O. Jones and J. K. Mathews found that when nitrosyl chloride and hydrogen are passed over reduced platinum cooled by a freezing mixture, the ammonium chloride produced contains 5 per cent. of hydroxylamine chloride. W. J. van Heteren found liquid chlorine and liquid nitrosyl chloride are miscible in all proportions. N. Boubnoff and P. A. Guye examined the f.p. of the binary system: $NOCl–Cl_2$, and found that the liquidus curve exhibits no maximum, and there is no sharp minimum at the eutectic temp., —109°, Fig. 99. The bending of the curve near —107° indicates the possible presence of an additive compound, *nitrosyl trichloride*, $NOCl_3$, which is highly dissociated even at —107°. M. Trautz and W. Gerwig's results are illustrated by Fig. 100. They found that mixtures kept for some time show a normal eutectic f.p. diagram with nitrosyl chloride and chlorine as solid constituents, but freshly prepared mixtures show a break in the liquidus at the composition of an unstable intermediate compound, *nitrosyl dichloride*, $NOCl_2$. M. Trautz and W. Gerwig found that mixtures kept for some time show a normal eutectic f.p. diagram with nitrosyl chloride and chlorine as solid constituents, but freshly-prepared mixtures show a break in the liquidus at the composition of an unstable intermediate compound, nitrosyl dichloride, $NOCl_2$. M. Trautz and H. Schlüter said that nitrosyl dichloride cannot be formed by the interaction of nitrosyl chloride and chlorine, but only from nitric oxide and chlorine; it is extremely unstable, and the equilibrium of the reaction by which it is formed lies very close to the left-hand side of the equation above. The heat of formation of nitrosyl dichloride is 7000 cals. (±700 cals.), and its formation and decomposition velocity constants are $1{\cdot}5\times10^{-5}$, respectively. H. O. Jones and J. K. Mathews found that with hydrogen sulphide at a low temp. in ethereal or petroleum soln., $NOCl+3H_2S=NH_4Cl+H_2O+3S$. M. Trautz and W. Gerwig measured the solubility of nitric oxide, in nitrosyl chloride, toluene, and pentane; E. V. Lynn and O. Hilton studied the action of nitrosyl chloride on heptane; W. Meisel, the action as *un agent de nitrosation* on organic compounds; P. A. Guye and G. Fluss, the action on selenium and sulphur to form the lower chlorides, Se_2Cl_2 and S_2Cl_2; W. Solonina, the action on amines: $R.NH_2+NOCl=RCl+N_2+H_2O$; and H. O. Jones and co-workers, the action on mercaptans—in ethereal soln., at —80°, a small proportion of hydroxylamine chloride is formed; with nickel as catalyst ammonium chloride is formed. J. J. Sudborough found that magnesium is not attacked at temp. up to 100°; silver, manganese, and nickel are slightly attacked when kept at 100° for many days;



FIGS. 99 and 100.—The Liquidus Curve of Mixtures of Nitrosyl Chloride and Chlorine.

under similar conditions, copper, gold, cadmium, thallium, lead, and platinum are attacked; and zinc, mercury, aluminium, tin, arsenic, antimony, bismuth, and iron are attacked in the cold. P. A. Guye and G. Fluss said that aluminium is not attacked in the cold, but above 500°, aluminium chloride is formed; silver-foil does not completely decompose the gas but finely divided silver does so at 400°–500°, forming silver chloride and nitric oxide; finely divided copper acts similarly. H. O. Jones and J. K. Mathews found that with palladium at ordinary temp. the metal chloride, nitric oxide, and nitrogen are formed; and at higher temp. ammonium chloride is produced. In agreement with J. J. Sudborough, V. Cuttica and co-workers found that nitrosyl chloride forms an unstable compound with cupric oxide which decomposes in air, forming cupric chloride; cuprous oxide or chloride forms **cuprous nitrosyl chloride,** $Cu_2Cl_2.NOCl$; thallous oxide forms **thallous nitrosyl chloride,** $2TlCl.3NOCl$, which is moderately stable in air, but in vacuo it forms thallosic chloride. R. Weber observed that nitrosyl chloride unites with the aluminium, titanium, antimonic, stannic and ferric chlorides. H. Gall and H. Mengdehl found that nitrosyl chloride reacts with the metal halides, forming primarily an addition product, which may be stable or may become transformed into the compound of nitric oxide and the higher chloride by transference of the chlorine atom from the nitrosyl chloride to the metal. If the latter compound is unstable, nitric oxide is evolved, and the residual higher chloride may unite with nitrosyl chloride. Thus, at —10°, manganous and nitrosyl chlorides form **manganese nitrosyl trichloride,** $MnCl_3.NO$, which is decomposed by water with the evolution of nitrous fumes, and when heated furnishes manganous chloride, chlorine, and nitric oxide; cuprous chloride similarly forms **copper nitrosyl dichloride,** $CuCl_2.NO$, which gives off nitric oxide when heated, and yields a dark blue soln. with acetone or alcohol resembling that obtained by W. Manchot by the action of nitric oxide on a soln. of a cupric salt. Sublimed ferrous chloride furnishes **ferric nitrosyl chloride,** $FeCl_3.NOCl$, obtained by J. J. Sudborough, and this is assumed to be a secondary product since $FeCl_3.NO$ is formed as an intermediate product; H. Rheinboldt and R. Wasserfuhr gave 128° for the m.p. Antimony trichloride yields **antimonic nitrosyl chloride,** $SbCl_5.NOCl$, m.p. about 170°; **bismuth nitrosyl chloride,** $BiCl_3.NOCl$, m.p. 115°–120°; aluminium chloride gives **aluminium nitrosyl chloride,** $AlCl_3.NOCl$, m.p. 108°-110°; and mercurous chloride gives **mercuric nitrosyl chloride,** $HgCl_2.NOCl$. W. Hampe, and V. Thomas represented the complex salt formed with stannic chloride by $3SnCl_4.4NOCl$, but R. Weber, A. Bäyer, S. M. Jörgensen and W. J. van Heteren agree that **stannic nitrosyl chloride** has the composition $SnCl_4.2NOCl$, which, according to H. Rheinboldt and R. Wasserfuhr, melts at about 188°. Similarly, **plumbic nitrosyl chloride,** $PbCl_4.2NOCl$, was prepared, as well as **titanic nitrosyl chloride,** $TiCl_4.2NOCl$, which did not melt below 220°. J. J. Sudborough prepared complex compounds with cuprous, auric, zinc, titanous, ferric, antimonic, bismuth, and platinum chlorides. The nitrosyl chlorides of the other metal chlorides were not stable at ordinary temp. E. V. Lynn and co-workers found that nitrosyl chloride acts on *n*-heptane in light; it also reacts with toluene in light, but not with benzene. R. H. Pickard and H. Hunter examined the action of nitrosyl chloride on nonanol; and O. Diepenbruck, on mercaptan and mercaptides. I. Guareschi found that nitrosyl chloride is readily absorbed at ordinary temp. by soda-lime or potash-lime. A. C. Girard and J. A. Pabst used nitrosyl chloride for preparing nitroso-derivatives of organic compounds; and J. A. Wesener used it in the bleaching of flour. The Badische Anilin- und Sodafabrik constructed containing vessels magnesium alloys. For *nitrosyl perchlorate, vide* **2.** 19, 17.

As previously indicated, the twelfth-century Latin work *De inventione veritatis*, attributed to the eighth-century Arabian, Geber, obtained what is now known as *aqua regia*, and he stated that the liquid will dissolve gold. In the literature of the Middle Ages, frequent reference is made to a mixture of nitric and hydrochloric acids, or a soln. of a nitrate in hydrochloric acid, or of a chloride in nitric acid as a solvent for gold—*aqua regia, aqua regis, Königwasser, Goldscheidewasser,* and *l'eau régale;* and it has also been called *nitromuriatic acid,* and *nitrohydrochloric acid.*

The twelfth-century Albertus Magnus, in his *Compositum de compositis,* called it *aqua secunda* to distinguish it from nitric acid, which he called *aqua prima;* and Raymond Lully, in his *Testamentum novissimum,* called it *aqua salis ammoniaci,* and *salis nitri.* M. Odomar, in his *Practica ad discipulum* (*Theatrum chemicum,* Argentorati, 1659), called the acid *aqua calcinationis omnium metallorum,* and made it by distillation from a mixture of vitriol, saltpetre, and common salt. Basil Valentine, in his *Letztes Testament* (Hambourg, 1717), and J. R. Glauber, in his *Furnis novis philosophicis* (Amstelodami, 1648), described aqua regia. J. B. van Helmont, in *De flatibus* in his *Ortus medicinæ* (Amsterdam, 1648), alluded to the peculiar gas which is exhaled by aqua regia; and T. Bergman, in his *De attractionibus electivis* (Upsala, 1775), seems to have regarded aqua regia as a specific acid.

The usual way of making aqua regia is to mix one part of nitric acid with two to four parts of hydrochloric acid. According to J. J. Berzelius,[3] the mixture is unstable and soon becomes yellow owing to the production of chlorine and nitrogen oxides. The change takes place rapidly if the soln. be warmed. In a closed vessel the decomposition ceases as soon as the liquid is saturated with the gas, but in an open vessel, from which the chlorine can escape, the action continues until all the nitric acid, or all the hydrochloric acid is decomposed. If the liquid is heated until chlorine ceases to be evolved, it no longer dissolves gold; and further, a mixture of hydrochloric acid and liquid nitrogen peroxide does not dissolve gold; but J. L. Gay Lussac, and C. J. Koene said that it does dissolve that metal; C. J. Koene found a mixture of hydrochloric and nitrous acid does not form aqua regia. C. J. Koene found that a mixture of conc. hydrochloric and nitric acids reacts at 0°. N. A. E. Millon made the interesting observation that mixtures of hydrochloric and nitric acids can be made which are free from nitrous acid, and which at ordinary temp. neither decompose nor attack arsenic, antimony, platinum, or gold. The action, however, commences by gently heating the mixture or by adding a small proportion of potassium nitrite. The addition of chlorine has no effect. Consequently, he concluded that *the presence of nitrous acid—whether produced by the mutual decomposition of the two acids by heat, or by direct addition to the mixture—is necessary before aqua regia can dissolve the noble metals.*

The products of the decomposition, and the nature of aqua regia, have been studied by H. Davy, A. Baudrimont, J. L. Gay Lussac, W. A. Tilden, and H. Goldschmidt. The peculiar properties of aqua regia were stated by H. Davy to be due to the presence of what he called *chloronitrous acid,* a compound of equal vols. of nitric oxide, and chlorine. A. Baudrimont heated a mixture of nitric and hydrochloric acid (2 : 3 by wt.) at 82°, and obtained the red gas which attacked gold, platinum, arsenic, and antimony, but not phosphorus; it condensed to a red liquid; and at 0°, water dissolved 121 times its vol. of gas. A. Baudrimont called this product *chloronitric acid,* and represented it by the symbol $N_2O_3Cl_4$. It was probable that dissolved chlorine was present in A. Baudrimont's product, and the *rôle* played by chlorine in aqua regia is ignored. Both H. Davy, and J. J. Berzelius had previously stated that the solvent action of aqua regia on gold is due to the presence of chlorine. J. L. Gay Lussac found that at the temp. of boiling water, aqua regia gives off a gas which condenses to a lemon-yellow liquid which he called *l'acid chlorhypoazotique,* or *hypochloronitric acid,* $N_2O_2Cl_4$. Its formation in modernized symbols was represented: $2HNO_3+6HCl=N_2O_2Cl_4+4H_2O+Cl_2$; it was further assumed that hypochloronitric acid is immediately decomposed by water, $N_2O_2Cl_4+2H_2O=N_2O_4+4HCl$. J. L. Gay Lussac also found that the lemon-yellow liquid also contained what he called chloronitrous acid, and which is now called nitrosyl chloride (*q.v.*). Consequently, he inferred that the products of the interaction of nitric and hydrochloric acid are chlorine, nitrosyl chloride, nitrosyl dichloride, and water; and that *the peculiar action of aqua regia on the metals is due to the chlorine liberated by its decomposition—the nitrosyl chlorides pass off as they do when the liquid alone is heated.* W. A. Tilden represented the reaction between nitric and hydrochloric acids by $3HCl+HNO_3=NOCl+Cl_2+2H_2O$; and this was confirmed by H. Goldschmidt, and G. Lunge and L. Pelet.

According to E. Briner, in a closed system, the reaction $HNO_3+3HCl\rightleftharpoons NOCl+Cl_2+2H_2O$ is reversible; the equilibrium press. at 0° is 2·84 atm., and at 20·5° to 21° it is 5·1 atm. Within these limits of temp., the system is univariant, having three phases and two independent components. This system is called *l'eau régale stabilisée*—that is, *stabilized aqua regia.* One liquid phase consists of nitrosyl chloride and chlorine in equilibrium with the aq. phase, which contains, in addition to the original acids, some chlorine and nitrosyl chloride. The gaseous phase contains all the constituents of the system. If the acids used are too dil. the phase consisting of the liquefied gases does not exist, and the equilibrium press. diminishes as the dilution increases. When the two conc. acids are mixed there is first a rapid rise of several degrees in the temp., which then descends steadily and remains constant at about 2° below the original temp. of the acids. The preliminary rise in temp. is due to the action of the hydrogen chloride on the water of soln. of the nitric acid. Taking into account the heats of soln., the heat of the reaction, using 37 per cent. hydrochloric acid and 70 per cent. nitric acid, is −20 Cals., and if the dilution of the acids is doubled, the value is −27 Cals. R. Heberlein confirmed these observations on *l'eau régale stabilisée,* for in the presence of the three phases, the electrical conductivity is constant for a given temp. whatever be the proportions and concentrations of the nitric and hydrochloric acids. This is characteristic of a univariant system. The stabilized aqua regia is therefore *un système tampon* for each kind of ion represented in the system. E. Briner gave 2·84 atm. for the vap. press. at 0°; and 5·1 atm. at 20°. The sp. conductivity of the non-aqueous layer is a maximum 0·324 mho at 0° after 24 hrs.

According to J. L. Gay Lussac, aqua regia prepared by mixing one part of nitric acid with two or three parts of hydrochloric acid is a yellow, fuming, highly corrosive liquid which is used for dissolving in hydrochloric acid those metals which have but a feeble affinity for oxygen. When copper, silver, mercury, phosphorus, arsenic trioxide, or ferrous chloride is treated with aqua regia, nitric oxide is formed: $3Cu+2HNO_3+6HCl=3CuCl_2+4H_2O+2NO$; tin, and the metals which decompose water readily give off no gas, but form ammonium chloride; and stannous chloride furnishes nitrous oxide. G. Bunge said that the vapour of aqua regia generally behaves towards organic compounds like free chlorine. F. Leblanc used aqua regia in Bunsen's cell—1. 16, 5; and A. K. Fedoroff recommended it for the sterilization of potable waters.

According to H. H. Landolt,[4] reddish-brown fumes are evolved during the action of conc. nitric acid on potassium bromide, and when condensed by cooling the product is possibly a mixture of nitrosyl bromide and dibromide. If nitric oxide be passed into bromine cooled between −7° and −15°, **nitrosyl bromide,** NOBr, is formed. E. Moles showed that the product always contains a slight excess of bromine. W. A. Tilden did not obtain this compound by treating nitrosyl chloride with potassium bromide, but rather obtained a heavy black liquid resembling bromine, while nitric oxide was evolved. He also said that two other bromides are produced, $NOBr_2$ and $NOBr_3$, and that nitrosyl bromide is to be separated from these by fractional distillation; but O. Fröhlich showed that distillation separates nitrosyl bromide and bromine; the two higher bromides are simply soln. of bromine in nitrosyl bromide at this temp. A. C. Girard and J. A. Pabst obtained nitrosyl bromide by the action of sodium bromide on nitrosyl sulphonic acid, $NO_2.HSO_3$. H. H. Landolt described nitrosyl chloride as a dark brown liquid which begins to boil at −2°, furnishing a vapour which is a mixture of nitrosyl bromide and nitric oxide, and the former constituent condenses on cooling; if the temp. be 20°, the residue contains 81·1 per cent. of bromine and corresponds with $4NOBr=2NO+N_2O_2Br_4$; and at a higher temp., the $N_2O_2Br_4$ is decomposed. S. Dushman, and M. Trautz and V. P. Dalal studied the equilibrium conditions in the reaction $2NO+Br_2=2NOBr$ at temp. between −15° and 15°, and with the bromine at 11–26 mm. press., and the nitric oxide, at 11–12 mm. press. At higher temp., the nitrosyl bromide decomposes, and at lower temp., bromine condenses on the glass containing vessel. The reaction appears to be of the third order, with the velocity constant between $0{\cdot}9\times10^{-10}$ and $1{\cdot}6\times10^{-10}$; and $\log K = -9416/4{\cdot}573T + 2{\cdot}5 \log T + 1{\cdot}59$. The temp. coeff. is too small to be determined with certainty. It is thought that the reaction was complicated by the concurrent or superimposed reaction $NO+Br_2 \rightleftharpoons NOBr_2$, which comes to equilibrium very quickly, and $NOBr_2+NO \rightleftharpoons 2NOBr$, which is measurable. In studying the equilibrium between −15° and 330°, with the bromine between 13 and 500 mm. press., and the nitric oxide between 28 and 900 mm. press., it was found that equilibrium is rapidly attained. With the bromine below 50 mm. press., and above 140°, the amount of tribromide formed is negligibly small, and the reaction is $2NO+Br_2=2NOBr$, with the velocity constant $1{\cdot}1\times10^{-10}$ at −15°—*vide supra*, nitric oxide and bromine. The fusion curve, Fig. 101, shows that the m.p. of nitrosyl bromide is about −55°. The results neither confirm nor deny the existence of a dibromide. The heat of formation of nitrosyl bromide is estimated to be between 9000 and 10,500 cals. The observed value is $2NO+Br_2=2NOBr+9416\pm500$ cals. It is concluded that with liquid mixtures of bromine and nitrosyl bromide, the chief product is the tribromide; in gaseous mixtures rich in bromine at moderate temp., the dibromide; and under other conditions, nitrosyl bromide and its dissociation products. H. W. B. Roozeboom measured the vap. press. of mixtures of nitrosyl bromide and bromine, but obtained no evidence of the existence of the higher bromides; he found that the vap. press. with 1·0, 0·9, and 0·79, 0·68, 0·60, and 0·42 mol of nitric oxide per mol of bromine was respectively 889, 700, 631, 545, 491, and 401 mm. Unlike M. M. P. Muir, he observed no sign of a discontinuity. M. Trautz and V. P. Dalal gave for the vap. press. of nitrosyl bromide :

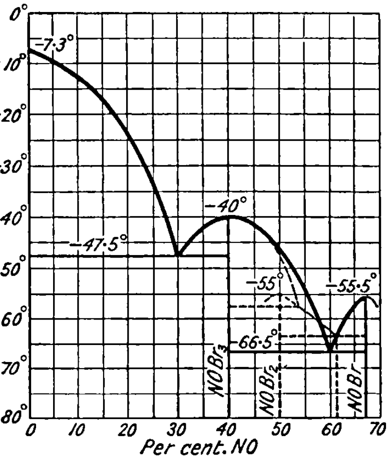


FIG. 101.—Melting-point Curve of Mixtures of Nitric Oxide and Bromine.

	−57·5°	−50°	−40°	−30°	−20°	−10°
Vap. press. .	327	334	347	384	472	693 mm.

The heat of vaporization is 6242 cals., and the critical temp., 210°. H. H. Landolt found that nitrosyl bromide sinks in cold water, and remains unchanged, but at 14°, bubbles of nitric oxide arise. The vapour attacks leaf-gold and mercury, forming the metal bromides. A. Kiss said that in the reaction between nitrosyl bromide and chlorine, no alteration is brought about by carbon dioxide. L. G. de Koninck found that nitrosyl bromide is hydrolyzed by a soln. of potassium hydroxide. M. Trautz and V. P. Dalal give : $2KOH+NOBr+Aq.=Aq.+KBr+KNO_2+H_2O+28{\cdot}658$ Cals. L. G. de Koninck said that with mercuric oxide, mercuric bromide and nitrous acid are formed; and that it behaves like nitrogen trioxide towards aniline. E. Briner found that mixtures of nitric acid and hydrobromic acids behave like mixtures of nitric and hydrochloric acids, forming a univariant system with vap. press. 0·25 atm. and 0·50 atm. respectively at 0° and at 16°.

According to H. H. Landolt, if nitrosyl bromide be gradually heated to about 30°, the residue which remains contains from 82·64 to 83·64 per cent. of bromine. This corresponds with **nitrosyl dibromide,** $N_2O_2Br_4$, or $NOBr_2$. He called it *Bromuntersalpetersäure*. The product is very dark brown, and resembles bromine ; it begins to boil at about 46°, and then partially decomposes into nitrosyl bromide. W. A. Tilden could not make this compound, and, as indicated above, O. Fröhlich regarded it as a soln. of bromine in nitrosyl bromide. As indicated above, M. Trautz and co-workers consider that the dibromide is present in gaseous mixtures of nitrosyl bromide and bromine; and the evidence obtained from the f.p. curve is indecisive. There is possibly a dibromide with the m.p.—55°, Fig. 101. H. W. B. Roozeboom said that the vap. press. of a soln. of nitric oxide in bromine, in the proportions, $NOBr_2$, is 601 mm. at —10°, 631 mm. at —8°, 729 mm. at —4°, and 889 mm. at 0°. If gas be allowed to escape at 0°, the proportion of bromine in the residue increases, and the vap. press. decreases. H. H. Landolt said that in the presence of water the dibromide absorbs oxygen: $2NOBr_2+3H_2O+O=4HBr+2HNO_3$; and the dibromide sinks in water, and is rapidly hydrolyzed to hydrobromic acid and nitrogen peroxide.

According to H. H. Landolt, if nitric oxide be passed into well-cooled bromine until the product is decolorized when shaken with water, **nitrosyl tribromide**, $NOBr_3$, is formed; and M. M. P. Muir obtained a similar product by the action of nitric oxide on bromine at different press. H. H. Landolt obtained it by distilling nitrosyl bromide or nitrosyl dibromide at 40°–55°. O. Fröhlich regarded it as a mixture of nitrosyl bromide and bromine. M. Trautz and V. P. Dalal showed that this compound is present in liquid mixtures of nitric oxide or nitrosyl bromide and bromine as indicated on the m.p. diagram, Fig. 97. They found the equilibrium constant for $2NO+3Br_2\rightleftharpoons 2NOBr_3$ to be $2{\cdot}1\times10^2$ at —14·6°, and $7{\cdot}5\times10^5$ at 80°; or $\log K_p=-5287T^{-1}+7{\cdot}5\log T+5{\cdot}15$ mm. At about 22°, the heat of formation of $NOBr_3$ is between 22,000 and 27,000 cals.; the observed value is $2NO+3Br_2=2NOBr_3+24{,}182\pm800$ cals. They obtained for the equilibrium constant of $NOBr+Br_2\rightleftharpoons NOBr_3$, $\log K=-1614T^{-1}+2{\cdot}5\log T+1{\cdot}78$ mm. H. H. Landolt gave 2·628 for the sp. gr. of the liquid tribromide at 22·6°; and M. Trautz and V. P. Dalal, 2·637 at 20°/4°. Its m.p. is —40°. The dark brown, almost opaque liquid begins to boil at 32° with partial decomposition. H. H. Landolt said that if rapidly heated, the tribromide can be distilled almost unchanged; when slowly distilled, an excess of nitrogen oxides escapes with the earlier fractions and bromine finally remains. The tribromide is rapidly decomposed when shaken with water: $NOBr_3+2H_2O=HNO_3+3HBr$; it dissolves in ether, and is decomposed slowly by absolute alcohol; it is decomposed in contact with silver or mercuric oxide, forming the metal bromide, nitrogen peroxide, and oxygen. Powdered sodium antimonide strewn in the vapour is inflamed. R. L. Datta and N. R. Chatterjee found that a mixture of nitric and hydrobromic acids reacts with many organic compounds giving nitrosyl tribromide, etc.

As indicated in connection with iodine tetroxide, N. A. E. Millon[5] observed the formation of what he considered to be *nitroso-iodic acid*, and H. Kämmerer what he considered to be *iodine dinitrosyl tetroxide*, $I_2O_4(NO)_2$, or maybe O : I.O.NO, by treating iodine with nitric acid, or nitrosylsulphuric acid. The yellow powder was considered by H. Kappeler to be *iodine nitrate*, $I.NO_3$, *vide* 2. 19, 9. E. Briner said that mixtures of nitric and hydriodic acids do not form a univariant system like stabilized aqua regia, for the iodine produced as a result of the primary reaction is oxidized to iodic acid, with the evolution of nitric oxide.

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§ 48. Nitroxyl or Nitryl Halides

According to H. Moissan and P. Lebeau,[1] a white solid is formed when nitric oxide is passed into an excess of fluorine at the temp. of liquid oxygen; as the temp. rises, the solid melts to a colourless liquid, and if a U-tube at —80° is attached to the containing vessel, a colourless liquid is condensed. The admixed fluorine can be removed by two rectifications, and there remains **nitroxyl fluoride,** or *nitryl fluoride*, NO_2F. This compound is a colourless, fuming gas at ordinary temp., and it attacks the mucous membrane, producing painful and persistent irritation. Its sp. gr. lies between 2·17–2·31 at 0°, the mean value is 2·24 ; its b.p. —63·5° ; and its m.p., —139°. Nitroxyl fluoride is very active, chemically, and it reacts with many metals at ordinary temp. It does not react with hydrogen, in the cold ; but it is hydrolyzed by water: $NO_2F+H_2O=HNO_3+HF$. The reaction is quantitative, and was utilized in analyzing the gas. Nitroxyl fluoride does not react with fluorine, or chlorine in the cold, but with dry iodine it forms iodine pentafluoride. It liberates the halogen from the iodides and bromides. It does not react with sulphur, selenium, or nitrogen at ordinary temp., but it reacts with phosphorus, arsenic, and antimony. It does not react with amorphous carbon even at dull redness. It readily reacts with many organic compounds like alcohol, ether, chloroform, carbon tetrachloride, and turpentine; with benzene it forms nitrobenzene and a volatile product which attacks the eyes. It reacts energetically with silicon, and attacks glass at ordinary temp. ; it also reacts at ordinary temp. with the alkali metals, the metals of the alkaline earths, mercury, aluminium, thorium, iron, and boron.

C. W. Hasenbach [2] made **nitroxyl chloride,** or *nitryl chloride*, NO_2Cl, as a pale yellowish-brown gas, by passing a mixture of chlorine and nitrogen peroxide through a strongly heated tube. A. Exner used this process. Nitroxyl chloride is also obtained from a mixture of hydrogen chloride and nitrogen peroxide. A. W. Williamson prepared it by the action of chlorosulphonic acid on nitric acid: $(HO)ClSO_3+HNO_3=NO_2Cl+H_2SO_4+H_2O$. The colourless vapour is said to react with water, forming nitric and hydrochloric acids. E. Bamberger prepared nitroxyl chloride by A. W. Williamson's method; and N. Zuskine, by the action of phosphorus pentachloride on nitric acid. M. Odet and L. Vignon obtained what they considered to be nitroxyl chloride by passing a slow current of dry chlorine over silver nitrate at 95°–100°, and passing dry carbon dioxide through the condensate to remove free chlorine ; and also by the action of phosphoryl chloride on lead or silver nitrate. A. Exner used M. Odet and L. Vignon's process. H. Schiff dropped conc. nitric acid on phosphorus pentachloride, and found that hydrogen chloride is evolved together with a red liquid condensate. When this is heated, phosphoryl chloride and yellowish-brown fumes—probably nitroxyl chloride—were said to be formed. J. Heintze heated nitrogen peroxide with potassium chlorochromate, and claimed that nitroxyl chloride was formed. M. Odet and L. Vignon said that the brownish-yellow gas condenses to a pale yellow liquid which does not solidify. R. Muller found the sp. gr. at 14° to be 1·32; and the vapour density, 2·52–2·62. M. Odet and L. Vignon said that the liquid does not freeze at —31°, and that its b.p. is 5°. The chloride becomes dark green in contact with ice, and decomposes with water, forming nitric and hydrochloric acids, without giving off gas. Silver nitrate converts it into silver chloride and nitric anhydride, and R. Müller said that it forms platinum chloride in contact with platinum. E. Bamberger studied its action on aniline; and N. Zuskine on magnesium alkyl halides.

There are doubts about the individuality of nitroxyl chloride. F. Meissner, A. Gutbier and J. Lohmann, and W. C. Williams could not make it by the above methods, and A. Geuther said that its existence is not very probable because it is not produced by the action of phosphorus pentachloride on liquid nitrogen peroxide. C. W. Hasenbach claimed to have made **nitroxyl bromide,** or *nitryl bromide*, NO_2Br, by the action of bromine on nitrogen peroxide ; and J. Heintze, by the action of nitrogen peroxide on potassium bromochromate, but these statements have not been verified. N. Zuskine, however, reported this compound to be formed when bromine vapour saturated with nitrogen peroxide, at 200°–250°, is passed through a tube filled with bone-ash. C. W. Hasenbach could not prepare **nitroxyl odide,** or *nitryl iodide*, NO_2I, by the action of nitrogen peroxide on iodine.

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§ 49. Nitrogen Sulphides or Sulphur Nitrides

The normal sulphide N_4S_3 is not known, but higher sulphides have been prepared. Probably sulphur is the positive and nitrogen the negative constituent, and it can be called *sulphur nitride*. In 1835, W. Gregory [1] reported an impure nitrogen sulphide to be formed by slowly dropping sulphur chloride into aq. ammonia in excess, and allowing the mixture to stand until the red product becomes yellow. The yellow substance dissolves in boiling alcohol, and as the soln. cools, it deposits crystals of sulphur; the conc. of the mother-liquor yields colourless crystals of nitrogen sulphide with a composition corresponding approximately with NS_6. M. J. Fordos and A. Gélis considered the alleged sulphide was an allotrope of sulphur insoluble in carbon disulphide; more probably it was **nitrogen sulphide,** or **nitrogen tetrasulphide,** N_4S_4, contaminated by much sulphur. E. Soubeiran obtained a sulphide contaminated by less sulphur than that of W. Gregory by the action of ammonia on the so-called sulphur dichloride, SCl_2. The product was treated with cold water which dissolved ammonium chloride and sulphide, leaving the nitrogen sulphide as a residue. This was rapidly washed with cold water, then with alcohol, and dried over sulphuric acid in vacuo. E. Soubeiran's product has a composition corresponding with N_2S_3; but A. Laurent supposed that it contained hydrogen, and had the empirical composition HNS.

The compound is endothermal, and therefore M. Berthelot and P. Vieille said that it must be prepared by indirect processes. Ammonia is the source of the nitrogen, and the sulphur can be obtained from the element, carbon disulphide, thionyl chloride, or sulphur chloride, S_2Cl_2. M. J. Fordos and A. Gélis passed dry ammonia into a soln. of one vol. of brown sulphur in 8–10 vols. of carbon disulphide until the red precipitate dissolved, forming a yellow soln.; the ammonium chloride was separated by filtration. The spontaneous evaporation of the clear liquid yields crystals of nitrogen sulphide and later of sulphur. The reaction can be represented $6SCl_2+16NH_3=N_4S_4+2S+12NH_4Cl$. R. Schenck passed dry ammonia into a soln. of sulphur chloride in benzene cooled by a freezing mixture; H. B. van Valkenburgh and J. C. Bailar used a soln. of 150 c.c. of dry ether and 5 c.c. of sulphur monochloride. The precipitate contains sulphur, nitrogen sulphide, and ammonium chloride. O. Ruff and E. Geisel, S. A. Vosnessensky, and F. P. Burt and F. J. Usher extracted the sulphide with dry benzene in Soxhlet's apparatus. A. K. Macbeth and H. Graham used ammonia and sulphur monochloride in chloroform soln.: $6S_2Cl_2+16NH_3=N_4S_4+12NH_4Cl+4S_2$. F. E. Francis and O. C. M. Davis thus describe the mode of preparation:

> The sulphide is best prepared by passing ammonia into a 10–15 per cent. soln. of sulphur dichloride in benzene. When the ordinary chloride is employed, the yield is much smaller. A rapid current of the dry gas is passed into the soln. until red fumes appear, the flask in which the operation is being conducted is then cooled, and on maintaining the current for a short time the reaction is completed. After filtering off the ammonium chloride formed, the soln., on evaporation, deposits long, orange-red prisms of nitrogen sulphide. This is a beautifully crystalline substance, and may be readily purified by recrystallization from either boiling benzene, toluene, or carbon disulphide.

F. P. Burt and F. J. Usher finally purified the sulphide by sublimation in vacuo over silver-gauze at 100°. Some nitrogen sulphide can be recovered from the mother-liquor. R. Schenck obtained a 44 per cent. yield, and he said that the resulting sulphide is so explosive that it is best kept in paper boxes ; the friction of the stopper of a glass bottle may cause an explosion. O. Ruff and E. Geisel consider R. Schenck's method to be the best mode of preparation, and believe that sulphur tetrachloride is the active agent concerned in the reaction: $12SCl_4+16NH_3=3N_4S_4+48HCl+2N_2$. A. Michaelis obtained nitrogen sulphide by the action of ammonia on thionyl chloride. The sulphide was extracted by carbon disulphide and crystallized from the soln. A 10 per cent. yield was obtained. O. Ruff and E. Geisel obtained nitrogen sulphide by the action of ammonia on a soln. of carbon disulphide in benzene. According to O. Ruff and E. Geisel, hydrogen sulphide and nitrogen sulphide are formed by the action of sulphur on liquid ammonia according to the equation $10S+4NH_3=6H_2S+N_4S_4$—*vide supra,* sulphammonium. The hydrogen sulphide is completely precipitated as silver sulphide, and the blue colour of the sulphammonium is changed into the orange-red of a soln. of nitrogen sulphide in ammonia when silver iodide (12 mols.) is added to sulphur (10 atms.) dissolved in liquid ammonia. The nitrogen sulphide is isolated by evaporating the filtrate, heating the residue at 100° for two hours, and extracting with carbon disulphide. On evaporating the soln., crystals of the tetrasulphide were obtained. E. Divers and T. Haga found that the thermal decomposition of barium amidosulphonate furnishes some nitrogen sulphide : $4(NH_2.SO_3)_2Ba=4BaSO_4+8H_2O+2N_2+N_4S_4$.

Nitrogen tetrasulphide forms golden-yellow or yellowish-red, transparent, prismatic crystals, which, according to R. Schenck, appear in orange-red needles when crystallized from benzaldehyde. When nitrogen tetrasulphide is strongly cooled by liquid air, O. Ruff and E. Geisel found that its colour is pale yellow. The crystals belong to the monoclinic system, and, according to J. Nicklès, the angle of the prism of the rhombic crystals is approximately the same as that of monoclinic sulphur. According to G. F. H. Smith, the sublimed crystals have the appearance of cubes with truncated edges and corners. E. Artini gave for the axial ratios $a:b:c=0{\cdot}8806:1:0{\cdot}8430$, and $\beta=89°\ 20'$; and G. F. H. Smith, $a:b:c=0{\cdot}8879:1:0{\cdot}8480$, and $\beta=89°\ 37'$. The indices of refraction are 2·046 and 1·908 ; these values are near to those of monoclinic sulphur. E. Artini said that twinning usually occurs on the $(\bar{1}01)$- or (101)-plane. A. Michaelis gave 2·1166 for the sp. gr. of the crystals at 10° ; S. A. Vosnessensky, 2·2 ; M. Berthelot and P. Vieille, 2·22 at 15° ; and F. P. Burt and F. L. Usher, 2·20 at 24° if it has not been sublimed, and 2·24 at 24° if sublimed. According to M. J. Fordos and A. Gélis, E. Soubeiran found that with friction the compound becomes electrical and sticky. The crystals explode when struck—say in a mortar by a pestle, and also when suddenly heated. M. Berthelot and P. Vieille said that the tetrasulphide burns without detonation in contact with a hot body ; and they gave 207° for the temp. of explosion. R. Schenck said that the crystals can be melted at 178°, but M. J. Fordos and A. Gélis found that the crystals sublime at 135°, and melt at 150° with a slow development of gas ; they explode at 160° with a feeble flash, forming nitrogen and sulphur. C. Hoitsema observed that at 170° the tetrasulphide partly volatilizes and in part slowly decomposes into its elements. S. A. Vosnessensky showed that it melts at 179° ; the presence of sulphur lowers the m.p. ; sublimation occurs near the m.p., and at higher temp. an explosion occurs. F. P. Burt said that the vap. press. is appreciable at 100° ; and the tetrasulphide sublimes in vacuo without decomposition. F. E. Francis and O. C. M. Davis found that the temp. of decomposition is very definite at 185° ; W. Muthmann and co-workers obtained 178°. A. Andreocci gave 178°–179° for the b.p. M. Berthelot and P. Vieille found the compound is endothermal having the heat of formation —127·6 Cals. They found the press., in kgrms. per sq. cm., developed with charges of 0·1, 0·2, and 0·3 grm. of nitrogen tetrasulphide and mercury fulminate to be respectively 815 to 480 ; 1703 to 1705 ; and 2441 to 2700. The press. developed by the explosion of nitrogen sulphide are, as may be seen, very similar to those obtained with the fulminate in the two latter experiments. If the explosion detonated in its own volume, the press. would be double with the fulminate, but the rapidity of the decomposition being very different, the effects produced by the two substances, supposing them to be used as detonators or "fuses," would be very dissimilar. According to F. P. Burt and F. L. Usher, nitrogen sulphide is decomposed into its elements when sublimed in vacuo over silver-gauze at 360°, forming silver sulphide and nitrogen; and it also decomposed by passage over quartz-glass wool in a quartz-glass tube at a red-heat. According to H. B. van Valkenburgh and J. C. Bailar, the hydrolysis of nitrogen tetrasulphide with a large excess of boiling water yields a neutral soln. in which 21·3 per cent. of the sulphur is present as pentathionic acid, 40·6 per cent. as sulphurous acid, 38·1 per cent. as free sulphur, and all the nitrogen as ammonia.

The compound was analyzed by M. J. Fordos and A. Gélis, M. Berthelot and P. Vieille, and F. P. Burt and F. L. Usher with results in agreement with the empirical formula NS. The data obtained by R. Schenck from the effect of the sulphide on the f.p. of naphthalene; by W. Muthmann and A. Clever, on the b.p. of carbon disulphide; and by A. Andreocci, on the b.p. of benzene and chloroform—agree with the quadrupling of the simple formula so as to give N_4S_4. R. Schenck argued that the sulphur in the tetrasulphide is bivalent by analogy with the sulphur diamine, $S(NH_2)_2$, and since ammonia is always produced in the reduction of the tetrasulphide while hydrazine is never formed, he also supposed that the nitrogen atoms are directly united by a triple bond because of the analogy of the tetrasulphide with the diazo-compounds with respect to colour and explosiveness. These assumptions led to the subjoined graphic formula. O. Ruff and co-workers discredited the assumption that the sulphur is bivalent. They showed that whenever sulphur is the electropositive part of a mol., as in the sulphur halides, it may be quadri- or sexivalent, but never bi-valent. Arguments based on the bivalency of sulphur in SCl_2 are ill-founded because of the doubts as to the individuality of this chloride—it is considered to be a soln. of S_2Cl_2 in SCl_4. The argument as to the quinquevalency of nitrogen, based on the colour-analogy with the diazo-compounds, is of little value because the azo-compounds with tervalent nitrogen exhibit similar colours; and both azo- and diazo-compounds can be reduced to hydrazine. Hydrazine, however, cannot be formed from nitrogen tetrasulphide. Observations on the hydrolysis, the action of hydrochloric acid, the action of ammonia, and on the formation of the thiodiimides show that the total number of active valencies in the mol. exceeds twelve. There is nothing to show that nitrogen atoms are joined each to each in the mol., and the reduction products make it doubtful if the contained nitrogen atoms are more than tervalent. The sulphur atoms are at least tervalent, but since no such valency for sulphur is known, it is assumed that some sulphur atoms are united each to each. O. Ruff and E. Geisel therefore argued in favour of one of the two formulæ indicated above—preferably the latter. The production of nitrogen tetrasulphide from sulphur and liquid ammonia supports this view. S. A. Vosnessensky also favoured the latter, in harmony with the behaviour of the compound on hydrolysis, and with its action on hydrochloric acid: $N_4S_4+12HCL=4NH_3+4S+6Cl_2$. The formation of lead and mercuric *thiodiimides* is assumed to occur through the change from $S:S(:N.S{\equiv}N)_2$ into $N{\equiv}S.HN_2$, and $S:S(NH)_2$, and the former furnishes $N{\equiv}S.NiHg$, and the latter $S:S(:N)_2Pb$. S. A. Vosnessensky said that the formula does not explain the reaction: $N_4S_4+CH_3.COCl{\rightarrow}N_3S_4Cl$, etc., and the production of the compounds N_3S_4Br, $N_3S_4NO_3$, and N_3S_4CyS; and the reaction: $N_3S_4Cl+NH_3{\rightarrow}N_4S_4$, etc.

$$S<\begin{matrix}N & \equiv\equiv\equiv & N\\ & >S\ S< & \\ N & \equiv\equiv\equiv & N\end{matrix}>S$$

R. Schenck's formula.

$$N<\begin{matrix}S=N-S\\ \ddot{S}-N=\dot{S}\end{matrix}>N \qquad S=S<\begin{matrix}N.\equiv SN\\ N.\equiv SN\end{matrix}$$

O. Ruff and E. Geisel's formulæ.

F. P. Burt obtained what he regarded as a **blue allotropic nitrogen tetrasulphide** by passing the vapour of the ordinary sulphide under reduced press. over silver-gauze at 100°. There was formed a conspicuous sublimate of yellow sulphide, and further on, a faint blue film appeared. The blue film gradually increased in quantity and spread in both directions. Finally the colour became deep blue and almost opaque in transmitted light; and bronze with a metallic lustre in reflected light. Analyses agreed with $(NS)_n$. The blue sulphide was quite insoluble when boiled with several organic liquids which dissolve the yellow sulphide, such as ether, chloroform, benzene, or carbon disulphide. On shaking or warming a piece of the tubing in water, the film rapidly scaled off, and was slowly decomposed. On adding a few drops of bromine water, soln. was accelerated, and the resulting liquid gave a precipitate of barium sulphate when mixed with a soln. of barium salt. When another portion was warmed with a soln. of sodium hydroxide, ammonia was evolved. When heated in air, the substance was decomposed with the evolution of vapours having an odour somewhat like that of iodine. When heated in vacuum, the substance showed no signs of volatilizing at 100°, and it could be freed in this manner from any accompanying yellow sulphide. When a small quantity was heated in a melting-point tube, decomposition occurred without liquefaction, the substance turning yellow at about the m.p. of the yellow sulphide (188°).

M. J. Fordos and A. Gélis said that nitrogen sulphide has a feeble smell, and that it irritates the mucous membranes; A. Michaelis said that the smell does not appear until the substance is warmed to 120°. M. J. Fordos and A. Gélis found that the sulphide is decomposed by water; but it suffers a slow decomposition in contact with water, forming ammonia and ammonium thiosulphate and trithionate: $2N_4S_4+15H_2O=(NH_4)_2S_2O_3+2(NH_4)_2S_3O_6+2NH_3$; but M. Berthelot and P. Vieille said that the sulphide can be moistened, and dried at 50° several times without appreciable change. O. Ruff and E. Geisel found that when one part of the sulphide is shaken with eight parts of cold water in a sealed tube for 24 hrs., the liquid smells of ammonia, and a sulphite, sulphate, thiosulphate, and trithionate can be detected in the liquid. According to M. J. Fordos and A. Gélis, the reaction with a soln. of potassium hydroxide can be represented: $N_4S_4+6KOH+3H_2O=4NH_3+2K_2SO_3+K_2S_2O_3$—if the nitrogen sulphide be contaminated with sulphur, the red-liquor observed by E. Soubeiran is produced. O. Ruff and E. Geisel found that when hydrolyzed with alkali-lye, nitrogen sulphide furnishes sulphurous and thiosulphuric acids with a small proportion of hydrogen sulphide and possibly dithionic acid, but not sulphuric and trithionic acids as obtained during the hydrolysis with water.

According to E. A. Demarçay, if chlorine be passed into nitrogen sulphide suspended in chloroform, the sulphide dissolves with the evolution of heat producing an orange-red, then an olive-green, and finally a brownish-red liquid which, on cooling, furnishes large, pale yellow crystals with the empirical formula SNCl, but which W. Muthmann and E. Seitter represent as **nitrogen tetrachlorotetrasulphide,** $N_4Cl_4S_4$. Similar crystals were made by S. A. Vosnessensky, and A. Andreocci. E. A. Demarçay said that this chloride unites with nitrogen sulphide, forming a compound, $(SN)_3Cl$, or **nitrogen tetrachlorododecasulphide,** $(N_4S_4)_3Cl_4$. W. Muthmann and A. Clever, and S. A. Vosnessensky prepared nitrogen tetrabromotetrasulphide, $N_4Br_4S_4$, by the action of a soln. of bromine in carbon disulphide on nitrogen sulphide, and when exposed to the vapour of bromine, **nitrogen hexabromotetrasulphide,** $N_4S_4Br_6$. Both substances form **nitrogen dibromopentasulphide,** $N_4S_5Br_2$, when exposed to air. O. Ruff and K. Thiel observed that nitrogen sulphide is decomposed when heated in the presence of copper oxide, water, and hydrofluoric acid, forming thionyl fluoride, etc. According to A. Michaelis, dry hydrogen chloride reacts vigorously with warm nitrogen sulphide, forming ammonium chloride, and a red sublimate—probably $N_4S_4.SCl_2$; A. Andreocci obtained a pale yellow chloride by the action of dry hydrogen chloride on a soln. of nitrogen sulphide in benzene. O. Ruff and E. Geisel showed that dry hydrogen chloride gas at ordinary temp. forms a brown powder which does not change in vacuo; while if nitrogen sulphide be treated with two or three vols. of liquid hydrogen chloride at ordinary temp., in a sealed tube, the reaction which occurs may be represented: $N_4S_4+12HCl=4NH_3+4S+6Cl_2$—no free nitrogen is produced. Nitrogen sulphide with barium chlorate forms very explosive red crystals.

The action of hydrogen sulphide on nitrogen tetrasulphide in the presence of liquid ammonia has been discussed in connection with sulphammonium. The reaction was investigated by K. Rötgers. E. A. Demarçay studied the action of nitrogen tetrasulphide on the chlorides of sulphur—*vide infra,* thiotrithiazyl-compounds. M. J. Fordos and A. Gélis, and S. A. Vosnessensky obtained the complexes $N_4S_4.2SCl_2$; $N_4S_4.SCl_2$; and $3N_4S_4.2SCl_2$ by the action of sulphur chloride on a soln. of nitrogen sulphide in carbon disulphide. According to H. B. van Valkenburgh and J. C. Bailar, the prolonged passage of ammonia through an ethereal soln. of sulphur monochloride yields, after evaporation, a viscous liquid of offensive odour which does not lose ammonia on heating. A similar compound was obtained with selenium. Liquid ammonia gives a black solid when mixed with sulphur monochloride. H. Wölbling found that sulphur and selenium chlorides react with nitrogen sulphide very slowly. A. Michaelis found that dry ammonia does not react with nitrogen sulphide, and in ethereal soln., ammonia produces a white compound. The reaction was studied by H. Wölbling. S. A. Vosnessensky, and O. Ruff and E. Geisel said that nitrogen sulphide copiously absorbs dry ammonia, forming **nitrogen diamminotetrasulphide,** $N_4S_4.2NH_3$, as an orange-red product which, at ordinary temp., exercises a considerable vap. press. Liquid ammonia, at —40°, form the same compound, which is stable in vacuo at 0°. If a liquid ammonia soln. of nitrogen sulphide be heated for some hours in a sealed tube at 100°, a bluish-violet soln. is obtained which, on evaporating the ammonia, leaves nitrogen tetrasulphide as a residue. The soln. of nitrogen sulphide in liquid ammonia reacts with some metal oxides soluble in the same solvent, forming a series of coloured complexes. F. A. Smith measured the conductivity of soln. of the tetrasulphide in liquid ammonia. M. J. Fordos and A. Gélis said that nitric acid very slowly oxidizes nitrogen sulphide. E. A. Demarçay also studied the action of nitrogen sulphide on phosphorus and arsenic chlorides. O. Ruff and E. Geisel observed that no action occurred when a liquid ammonia soln. of nitrogen sulphide is treated with arsenic or antimony trichloride; nitrogen sulphide dissolves in arsenic trichloride, forming a slightly turbid soln., and in antimony trichloride, forming a clear, blood-red soln. H. Wölbling said that no complexes are formed with the phosphorus, arsenic, or antimony trichlorides. O. C. M. Davis, and H. Wölbling prepared the complex $N_4S_4.SbCl_5$.

According to M. J. Fordos and A. Gélis, nitrogen tetrasulphide is slightly soluble in alcohol, ether, and turpentine, while 100 grms. of boiling carbon disulphide dissolve 1·5 grms. of nitrogen sulphide ; and, according to A. Andreocci, it is soluble in benzene and in carbon tetrachloride. S. A. Vosnessensky gave for the solubility in grams per litre, in carbon disulphide, benzene, and alcohol:

	0°	10°	20°	30°	40°	50°	60°
CS_2 . .	3·705	6·845	9·391	13·188	16·887	—	—
C_6H_6 . .	2·266	4·260	6·301	8·692	11·107	13·721	17·100
C_2H_5OH .	0·645	0·830	1·050	1·271	1·478	1·640	—

R. Schenck said that when nitrogen tetrasulphide is added to a soln. of sodium ethoxide (4 mols.) in alcohol, the liquid acquires a colour which is purple-red by transmitted, and dark green by reflected light, gradually becoming violet and ultimately brown; this coloration is permanent in absence of water, but if water is added the soln. becomes yellow and acquires a most offensive odour. Absolute ether precipitates from the alcoholic soln. a substance which crystallizes in lustrous scales, and exhibits dichroism; it is excessively unstable, and the soln. in alcohol is red. W. Muthmann and A. Clever said that if a soln. of nitrogen tetrasulphide in carbon disulphide or carbon tetrachloride is heated under 5 atm. press., nitrogen pentasulphide is formed; if similarly heated to 110° with ether, no pentasulphide is produced, but a substance smelling like acetamide is produced; and if similarly heated to 125° with benzene, no pentasulphide is produced, but a substance with a smell like oleum absynthii is formed. W. Muthmann and E. Seitter obtained thiotrithiazyl-chloride by the action of acetyl chloride on nitrogen tetrasulphide. According to R. Schenck, nitrogen tetrasulphide is indifferent towards primary and secondary bases of the aromatic series and all tertiary bases. If the substance is covered with piperidine, heat is generated, ammonia and nitrogen being evolved, whilst the mass, on cooling, deposits thiopiperidine; the action proceeds quantitatively in accordance with the equation $3N_4S_4+24C_5H_{10}NH=12(C_5H_{10}N)_2S+8NH_3+2N_2$. When nitrogen tetrasulphide is heated for one hour with dimethylamine, and the product distilled, the fraction which boils below 100° is a colourless oil, which solidifies in a mixture of ice and salt; this substance is thiodimethylamine, crystallizing in lustrous leaflets having a disagreeable, irritating odour. Ethylamine acts on nitrogen tetrasulphide, producing tetraethylthiodiamine, $S(NEt_2)_2$. Nitrogen tetrasulphide converts benzylamine into polymerized benzonitrile—*i.e.* cyanophenine—ammonia and nitrogen are evolved; when, however, the generation of heat is checked, and excess of benzylamine is employed, the *thionamide* of thiobenzoic acid, S : CPh.N : S, is produced, crystallizing from ethylacetate in beautiful yellow prisms, melting at 104°–105°. Along with this, a liquid is formed which becomes deep red when exposed for some days to air; on acidification, ether extracts the colouring matter, which consists of dithiobenzoic acid. Cold phenylhydrazine is without action on nitrogen tetrasulphide, but on application of heat, there is a violent disengagement of ammonia and nitrogen, benzene, sulphur, and hydrogen sulphide being also produced. F. E. Francis and O. C. M. Davis studied the action of nitrogen tetrasulphide on various aromatic aldehydes—*e.g.* benzaldehyde, tolualdehyde, and anisaldehyde. H. Wölbling said that nitrogen sulphide does not form complexes with carbonyl chloride, or with ethyl bromide, ethylene bromide, or benzyl chloride.

E. A. Demarçay prepared complexes of nitrogen tetrasulphide with silicon, titanium, zirconium, and stannic chlorides; and O. C. M. Davis reported the formation of $N_4S_4.Ti_2Cl_6$; or $2N_4S_4.SnCl_4$; and $N_4S_4.MoCl_4$; and $N_4S_4.WCl_4$. H. Wölbling made $N_4S_4.TiCl_4$, and $2N_4S_4.SnCl_4$, but stannous chloride does not form a complex. According to O. Ruff and E. Geisel, soln. of the metal iodides and of nitrogen tetrasulphide in liquid ammonia give precipitates. Lead and mercuric iodides form the corresponding dithiodiimides (*q.v.*), but the other iodides do not yield definite compounds—*e.g.*, cadmium, bismuth, and chromium iodides—because they are not sufficiently soluble in liquid ammonia; silver and aluminium iodides, because the products are too soluble; calcium iodide, because the precipitate is difficult to filter; and potassium iodide, because the precipitate is too difficult to wash.

F. L. Usher found that the sublimation of nitrogen sulphide containing free sulphur over silver gauze at about 125° yields a film of a ruby-red compound which turns deep blue on keeping (½ hr.–2 days) or on warming at 50°, and behaves like blue nitrogen sulphide of F. P. Burt—*vide supra.* Nitrogen sulphide free from sulphur yields directly the blue compound, from which the ruby compound could never be obtained. These modifications are considered to be produced from different intermediate volatile nitrogen sulphides, the one giving rise to the ruby compound being formed by the decomposition of **nitrogen persulphide** or **nitrogen disulphide,** NS_2, by silver. Nitrogen persulphide is obtained as a dark red liquid, resembling bromine, and solidifying to a pale yellow solid at the temp. of solid carbon dioxide, by subliming nitrogen sulphide with sulphur at 125° in the absence of silver gauze. It has a penetrating odour like that of iodine and can be distilled unchanged in a vacuum. At the ordinary temp., it decomposes slowly into sulphur and yellow nitrogen sulphide. Water decomposes it into ammonium salts and free sulphur. It is more volatile than the sulphide N_4S_4; hydrogen sulphide decolorizes an ethereal soln. with the probable formation of a thio-acid of nitrogen.

According to W. Muthmann and A. Clever, **nitrogen pentasulphide,** N_2S_5, can be prepared by heating nitrogen tetrasulphide with pure carbon disulphide at 100° for two hours under a press. of five atms. A deep red soln. is obtained together with a yellowish-brown, amorphous precipitate ; the filtrate is distilled until the greater part of the carbon disulphide is separated, and the residue is allowed to evaporate at the ordinary temp. in vacuo. The red oily product, consisting of a mixture of the pentasulphide with sulphur, is triturated with perfectly dry ether as quickly as possible, when the greater portion of the sulphur remains undissolved. The residual sulphur is crystallized out by means of a freezing mixture at −25° and the filtrate allowed to evaporate in dry air ; finally, the last traces of ether are removed by allowing the product to remain over calcium chloride, and the residual red oil is filtered. The formation of the pentasulphide takes place according to the equation $N_4S_4+2CS_2=N_2S_5+S+2CNS$. If the product is pure and contains no sulphur, it crystallizes from a well-cooled soln. in ether in metallic tablets resembling iodine.

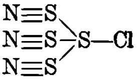
The amorphous by-product mentioned above, on analysis, gave numbers agreeing with the formula $C_3N_3S_3$; it is a very finely-divided, yellow powder, is extremely hygroscopic, and obstinately retains traces of carbon disulphide and nitrogen pentasulphide. It dissolves without alteration in concentrated sulphuric acid, and has properties similar to those of pseudocyanogen sulphide, $C_3N_3S_3H$.

The pentasulphide is also formed by heating a mixture of nitrogen sulphide and carbon tetrachloride, an amorphous black by-product being also formed containing carbon, nitrogen, sulphur, and chlorine ; this quickly decomposes on exposure to the air with evolution of sulphur dioxide. It is also produced by reducing with zinc dust thiotrithiazyl chloride, N_3S_4Cl, suspended in methyl alcohol ; and, generally, by the decomposition of nitrogen sulphide and its derivatives ; for instance, when nitrogen sulphide is exploded by friction, when the compounds of nitrogen sulphide with the halogens, or with nitrous acid, are boiled with water, and when nitrogen sulphide is heated cautiously with lead oxide. It is not, however, formed by heating nitrogen sulphide with ether or benzene at 110°–125° in a sealed tube. A. K. Macbeth and H. Graham found that some pentasulphide is formed in the action of sulphur monochloride on ammonia in chloroform soln.

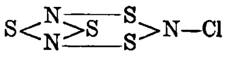
Nitrogen pentasulphide is a deep red, mobile liquid, which in thin layers appears transparent. It does not wet glass. Its sp. gr. is 1·901 at 18°. When cooled, it furnishes a crystalline, steel-grey mass, resembling iodine, and it melts at 10°–11°. Its odour resembles to some extent that of iodine, and it attacks the mucous membrane. If a little is put on the tongue it appears to have no taste, but it very soon develops a severe burn. The analysis corresponds with N_2S_5, and its effect on the f.p. of benzene corresponds with the same formula. Nitrogen pentasulphide is easily decomposed ; in summer, or in moist air, it very soon gives off gas, forming sulphur and nitrogen tetrasulphide. It decomposes when boiled at atm. press. into nitrogen and sulphur—at first the decomposition proceeds slowly with the evolution of nitrogen, but the pentasulphide soon detonates. At 10 mm. press., and about 50°, about 10 per cent. passes into nitrogen tetrasulphide, and 90 per cent. into sulphur and nitrogen. It is insoluble in water ; and when boiled with water, a small quantity distils undecomposed, and the remainder forms ammonia and sulphur. It is decomposed by a soln. of potassium hydroxide in a similar manner. When a minute quantity of an alcoholic soln. of potassium or sodium hydroxide is added to an alcoholic soln. of nitrogen pentasulphide, an intense but transient violet-red coloration is produced, and this reaction is so characteristic that the smallest quantity of the pentasulphide can be detected. When the pentasulphide is added to alcoholic potassium, a dark-coloured soln. is obtained, from which ether precipitates a yellow, crystalline compound ; this is probably a **nitrogen sulphonitrate,** which decomposes directly it is removed from the soln. With alcoholic alkali sulphides, it yields polysulphides and ammonia, and with hydrogen sulphide, ammonium polysulphide and sulphur. It is violently oxidized by concentrated nitric acid with formation of sulphuric acid ; and with dil. hydrochloric or sulphuric acid, it yields ammonium salts and sulphur. Nitrogen pentasulphide is soluble in most organic solvents—carbon disulphide dissolves 8–12 per cent. dependent on the temp. ; ether, 2–3 per cent. ; but it is sparingly soluble in benzene, alcohol, and chloroform. The soln. of the pentasulphide in these solvents is stable provided it is not exposed to light ; an ethereal soln. can be kept for months in darkness. In light, nitrogen tetrasulphide and sulphur are formed. The absorption spectrum of the soln. of the pentasulphide shows a broad band extending from the *D*-line into the blue.

There are three **nitrogen oxysulphides** whose constitution and mol. wts. are unknown, and therefore they have not been given a name. (1) When a soln. of nitrogen tetrabromotetrasulphide in carbon disulphide is treated with nitrogen peroxide, there is deposited a pale yellow powder consisting of microscopic prisms. Its composition approximates NSO_2 or $N_5S_6O_4$. It is fairly stable in air, but slowly decomposes, giving off nitrogen peroxide. It dissolves in cold water, and the soln. is neutral ; and when the soln. is warmed, a black substance is precipitated which soon begins to decompose. Alcohol gives a dark red soln. which evolves sulphur dioxide when boiled, and deposits a white crystalline substance. (2) If nitrogen dibromopentasulphide is treated with nitrogen peroxide in a similar way, yellow needles of a substance with the composition $N_4S_3O_6$ are formed. It decomposes with incandescence at the temp. of a water-bath ; it dissolves in cold water, and the aq. soln. decomposes when heated. (3) If nitrogen tetrasulphide be treated with a soln. of nitrogen peroxide in carbon disulphide, a white crystalline mass separates in a few hours. The composition approximates NSO_4. The crystalline plates are doubly refracting ; and they are deliquescent in air. They react with water with a hissing noise, and the evolution of nitric oxide : $NSO_4+H_2O=NO+H_2SO_4$.

In 1880, E. A. Demarçay found yellow microscopic crystals of what was considered to be the chloride of a univalent radicle N_3S_4 among the products of the action of yellow sulphur chloride on nitrogen sulphide. He called the radicle NS, *thiazyl*, and N_3S_4, **thiotrithiazyl.** He considered the radicle to be constituted with quadrivalent sulphur and tervalent nitrogen, so that the chloride became $(N:S)_3S.Cl$; while W. Muthmann and E. Seitter assumed the sulphur to be bivalent, and the nitrogen tervalent, $(SNS)_2N.Cl$, or



E. A. Demarçay's formula.



W. Muthmann and E. Seitter's formula.

The compound prepared by E. A. Demarçay was therefore **thiotrithiazyl chloride,** N_3S_4Cl. W. Muthmann and E. Seitter prepared this compound from nitrogen sulphide by the action of warm sulphur dichloride diluted with chloroform ; it is more conveniently prepared by heating nitrogen sulphide with acetyl chloride (4 parts) in a reflux apparatus for half an hour, when it is obtained as an intensely yellow, crystalline powder, exhibiting the properties attributed to it by E. A. Demarçay. On boiling the substance with alcohol during a short period, and treating the liquid with a few drops of alcoholic potash, an intense, violet-red coloration is developed, and does not immediately disappear on dilution with water. Ammonia gas is rapidly absorbed by the dry compound, which explodes violently after a few minutes ; if thiotrithiazyl chloride is suspended in chloroform and submitted to the action of the gas, the liquid becomes orange-red, and ammonium chloride and sulphide are produced, nitrogen sulphide being regenerated. According to E. A. Demarçay, if the sulphur chloride and nitrogen sulphide react in the cold, black crystalline dithiotetrathiazyl dichloride, $S_6N_4Cl_2$, is formed. It is dissolved by sulphuric acid, giving off hydrogen chloride, and is decomposed by heat ; $3S_6N_4Cl_2=4S_4N_3Cl+S_2Cl_2$. E. A. Demarçay prepared **thiotrithiazyl hydrosulphate,** $N_3S_4.HSO_4$, by the action of conc. sulphuric acid on the chloride, and precipitation by the addition of 4–5 vols. of acetic acid. The pale yellow needle-like crystals are stable provided moisture be excluded. E. A. Demarçay also made **thiotrithiazyl nitrate,** $N_3S_4.NO_3$. W. Muthmann and E. Seitter also obtained the latter by dissolving the chloride in conc. nitric acid, and evaporating the yellow liquid in vacuo. The resulting nitrate is very explosive, and crystallizes in sulphur-yellow, long, transparent prisms, and when preserved during some days becomes opaque and acquire the colour of sulphur dioxide mixed with oxides of nitrogen. The soln. in water is yellow and transparent, but becomes opaque in a few minutes, depositing a black substance mixed with much sulphur; a red liquid is obtained on boiling the compound with alcohol. **Thiotrithiazyl bromide,** N_3S_4Br, obtained by dissolving nitrogen sulphide and sulphur bromide (5 parts) in carbon disulphide, crystallizes in small, yellow needles; it is also formed when excess of bromine acts on thiotrithiazyl chloride in warm carbon disulphide, and is identical with the compound produced on exposing the tetrabromide of nitrogen sulphide to the action of moist air. The substance is stable in air, and when water is boiled with it, ammonium bromide, sulphur, and sulphurous anhydride are produced; hot dil. alkalis give rise to ammonia, along with alkali bromide, thiosulphate, and sulphate, and sulphide. **Thiotrithiazyl iodide,** N_3S_4I, is prepared by dissolving thiotrithiazyl chloride in ice-cold water and immediately adding excess of an ice-cold soln. of potassium iodide; it is a dark red, crystalline powder which decomposes spontaneously on exposure to the air, vapours of iodine being evolved. The compound is also obtained by acting on the chloride with iodine dissolved in methyl alcohol, but it invariably contains chlorine when prepared in this way. **Thiotrithiazyl thiocyanate,** N_3S_4CNS, is obtained by adding a soln. of potassium thiocyanate to an ice-cold soln. of thiotrithiazyl chloride or nitrate; it crystallizes in lustrous, bronze leaflets and resists the action of air. The salt dissolves somewhat readily in benzene and chloroform.

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§ 50. Amidosulphimic Acid and its Salts

The ammonia derivatives of sulphurous and sulphuric acids—forming respectively the monobasic sulphurous and sulphuric acids—include the amido-, the imido-, and the nitrilo-acids according as one, two, or all three atoms of ammonia are replaced by the sulphinic, HSO_2-radicle, or the sulphonic, HSO_3-radicle:

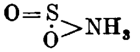
NH_3	$NH_2(HSO_2)$	$NH(HSO_2)_2$	$N(HSO_2)_3$
Ammonia.	Amidosulphinic acid.	Imidosulphinic acid.	Nitrilosulphinic acid.
NH_3	$NH_2(HSO_3)$	$NH(HSO_3)_2$	$N(HSO_3)_3$
Ammonia.	Amidosulphonic acid.	Imidosulphonic acid.	Nitrilosulphonic acid.

According to J. W. Döbereiner,[1] dry sulphur dioxide reacts energetically with dry ammonia, forming a pale brown mass, which is decolorized when treated with water, forming ammonium sulphite. H. Rose said that in whatever proportions the two gases are mixed, they always condense in equal vols., forming one homogeneous substance—*sulphitoammonia*—which is either yellowish-red and viscid, or red and crystalline; the product is very deliquescent dissolving in water without evolving ammonia. The soln. is neutral, and is at first yellow, but soon becomes colourless. The freshly prepared soln. gives reactions for ammonium sulphate and trithionate, and, to a less extent, for ammonium sulphite. Soln. of certain concentrations give a transient red coloration with hydrochloric acid. G. Forchhammer found the product contains some crystals which were assumed to be ammonium sulphate. He said the moist product is alkaline, and evolves ammonia. Alcohol extracts a substance which acquires temporarily a rose colour.

E. Divers and M. Ogawa found that if the gases are very thoroughly dried they do not combine at ordinary temp., but if the dried gases, with ammonia in excess, be mixed in a vessel cooled by a freezing mixture, the solid mass which is produced consists largely of ammonium amidosulphinate, $(NH_4)(NH_2.SO_2)$, mixed with other substances requiring more than 2 mols of sulphur dioxide to 3 mols of ammonia. If this product be warmed between 30° and 35° in a current of dry nitrogen or hydrogen, it contains no amidosulphinate, and gives up no sulphite to water. It then contains $N:S=1:1$ very nearly. If the temp. at which the gases are mixed does not rise above 30° or even 40°, the product contains very little sulphate, but if the temp. rises sufficiently high, much sulphate is formed. If prepared at the lower temp., trithionates are absent. F. Ephraim and H. Piotrowsky found that three different products are produced by the interaction of sulphur dioxide and ammonia: (i) with an excess of sulphur dioxide, amidosulphinic acid is always formed; (ii) with an excess of ammonia, ammonium amidosulphite; or (iii) a red product with the same ultimate composition, but with double the mol. wt. $2SO_2.4NH_3$, which is ammonium imidosulphinate, $NH_4.N:(SO_2NH_4)_2$.

M. Schumann observed that if the sulphur dioxide be in excess the compound $SO_2.NH_3$ is formed; and if the ammonia be in excess, $SO_2.2NH_3$ is formed. He described the compound $NH_3.SO_2$—previously called **amidosulphinic acid** or *amidosulphurous acid*—as a yellow, crystalline powder which is very hygroscopic. It is at once decomposed by water yielding a faintly acid soln. which, when treated with acids, evolves sulphur dioxide without the precipitation of sulphur. The freshly prepared soln. contains ammonium salts, and sulphuric, sulphurous, thiosulphuric, trithionic, and pentathionic acids: $4NH_3SO_2+2H_2O=(NH_4)_2SO_4+(NH_4)_2S_3O_6$; $NH_3SO_2+H_2O=NH_4HSO_3$; $4NH_4(HSO_3)=(NH_4)_2S_2O_3+2NH_4(HSO_4)+H_2O$; $10NH_3SO_2+6H_2O=(NH_4)_2S_5O_6+3(NH_4)_2SO_4+2NH_4(HSO_4)$. According to H. Rose, when the recently prepared soln. is boiled with some potassium hydroxide until ammonia ceases to be evolved, and hydrochloric acid is added, sulphur dioxide is evolved but no sulphur is precipitated. M. Schumann pointed out that if trithionates were present, such a treatment would form sulphites and thiosulphates with the deposition of sulphur. H. Rose found that when hydrochloric acid is added to the fresh soln., sulphur dioxide is given off, sulphur is deposited, and sulphuric acid remains in soln.; conc. sulphuric acid yields sulphur dioxide, but with a conc. soln., some sulphur is precipitated; and selenious acid gives a red precipitate of selenium with a fresh soln. of amidosulphinic acid, but not with a soln. which has been kept for some weeks. The freshly prepared soln. gives a precipitate of barium sulphate when treated with barium chloride. The fresh soln. is not affected by a soln. of copper sulphate at ordinary temp.; but, when heated, copper sulphide is precipitated; mercuric chloride gives a white precipitate, but if the amidosulphinic acid is in excess, black mercuric sulphide is precipitated; and with silver nitrate, the soln. behaves like a mixed soln. of a thiosulphate and trithionate, with a small proportion of silver nitrate; the white precipitate first formed redissolves; with a larger proportion, the precipitate is permanent, and then changes through yellow and brown to black. The black sulphide also contained some metallic silver, probably reduced by sulphurous acid. E. Divers and M. Ogawa, however, said the fresh soln. gives reactions which do not characterize trithionates—*e.g.* it may be acidified and left for hours without yielding more than traces of sulphur or sulphur dioxide; to obtain these in quantity the soln. must be heated under press. The absence of sulphate is considered to disprove the production of trithionate, since, as H. Rose himself has shown, sulphate and trithionate are complementary products of the decomposition. According to M. Schumann, if amidosulphinic acid be heated under dry carbon disulphide in a reflex apparatus, ammonia is evolved, and a dark red, crystalline sublimate with the composition and provisional name *trisulphitotetrammine*, $3SO_2.4NH_3$, is formed. This compound is very hygroscopic and yields a soln. in water similar to that of ammonium amidosulphinate. E. Divers and M. Ogawa consider this compound as a mixture of the decomposition products of ammonium amidosulphinate; and M. Schumann considers it is possibly *ammonium nitrilosulphite*, $N(SO_2NH_4)_3$.

The old ideas as to the nature of the compounds were somewhat vague. N. A. E. Millon, and G. Forchhammer supposed that the sulphur is combined either with amidogen, NH_2, or with nitrogen. H. Schiff regarded the compound $NH_3.SO_2$ as a *thionaminic acid*, $NH_2.SO_2H$; and it may be called *amidosulphinic* or *amidosulphurous acid*, and M. Schumann discussed the formula



$$O{=}\overset{\displaystyle S}{\underset{\displaystyle O}{\cdot}}{>}NH_3$$

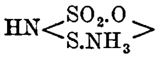
H. Schiff regarded $2NH_3.SO_2$ as ammonium thionaminate, $NH_2.SO.ONH_4$; while A. Michaelis and O. Storbeck represented some organic derivatives of $SO_3.2NH_3$ by a formula $(NH_2)_2S(OH)_2$; and E. Divers and M. Ogawa assumed that the compound is ammonium amidosulphite, $NH_4.N(SO_2.NH_4)_2$, and not $NH_2.SO.ONH_4$. On account of its feeble activity as a reducing agent, and its easy passage into ammonium sulphite or ethyl ammonium sulphite, it is supposed to be a sulphuryl rather than a thionyl compound—*vide infra*, sulphuryl amide.

According to M. Schumann, when potassamide is heated to 200° in an atm. of sulphur dioxide there is a violent reaction, with evolution of light and heat; the products are a mixture of the compounds $SO_2.NH_3$ and $SO_2.2NH_3$, and a residue containing potassamide, potassium, sulphur dioxide, and a small quantity of ammonia. Similar compounds are obtained by the action of sulphur dioxide on the anhydrous fatty amines, when brought into direct contact without the presence of a solvent at about $-6°$. Ethylamine yields **ethyl amidosulphinate,** $SO_2.NH_2Et$, which crystallizes in yellow scales and yields a colourless soln. in water containing the amine and sulphuric, sulphurous, thiosulphuric, trithionic, and pentathionic acids. **Dimethyl amidosulphinate,** $SO_2,NHMe_2$, obtained from dimethylamine, is a yellow, crystalline mass, and with water gives a faintly acid soln. which contains the amine and sulphuric, sulphurous, and thiosulphuric acids only.

Amidosulphinic acid is monobasic, and furnishes salts, **amidosulphinates** or *amidosulphates*. M. Schumann prepared **ammonium amidosulphinate,** $2NH_3.SO_2$, or $NH_4(NH_2SO_2)$, from a mixture of dry sulphur dioxide and an excess of dry ammonia in a flask cooled to $-5°$ to $-7°$. It furnishes red fragments and nodules which are crystalline aggregates. When exposed to air, it gradually changes to a white powder. It dissolves in water with the evolution of ammonia; and the soln. gives a transient red coloration when treated with acids. The freshly prepared aq. soln. contains ammonium salts and sulphuric, sulphurous, thiosulphuric, trithionic, and pentathionic acids. E. Divers and M. Ogawa obtained the salt by saturating sodium-dried ether with dry ammonia in a well-cooled flask, and then passing in a very slow current of dry sulphur dioxide while frequently agitating the contents of the flask. A rise of temp. was avoided as much as possible. The ether was decanted from the yellow solid into a second flask, and the ether adhering to the precipitate removed by a current of dry ammonia continued some hours, while the flask was still cooled by a freezing mixture. Caking of the salt should be avoided. Neither air nor hydrogen can be used for drying the salt; and the flask cannot be removed from the freezing mixture while the solid is moistened with ether, without the salt acquiring a yellow colour. When dried in an atm. of ammonia the salt is more stable, but it cannot be kept long at ordinary temp. without being discoloured by decomposition. Ammonium amidosulphinate is white and probably crystalline. For a possible explanation of the formation of the red colour of M. Schumann's product by the heat developed during the reaction of the compound gases, *vide infra.*

E. Divers and M. Ogawa said that ammonium amidosulphinate appears to be slightly volatile in a current of ammonia. It is very deliquescent, and, on exposure to the air, decomposes, losing ammonia. It dissolves in water, giving out heat and a hissing sound, and if dissolved by ice or enough ice-cold water, furnishes a soln. answering all the tests for pure ammonium sulphite. In this respect, it is quite unlike ammonium amidosulphate or carbamate, since even the latter salt gives at first no precipitate with calcium chloride, which at once precipitates all sulphite from the new salt. When the salt is much decomposed, its soln. gives other reactions besides those of a sulphite. In anhydrous alcohol, it dissolves freely, evidently as ethyl ammonium sulphite; it is also slightly soluble in dry ether. It soon begins to change, and then assumes an orange colour, even at the common temp. When ammonium amidosulphinate is heated to 30°–35° in a dry atm., whether by the heat of reaction or by external heat, it is decomposed into an indistinctly crystalline, white solid, and a much smaller quantity of a coloured, effervescing liquid, part of which drains to the bottom of the vessel; after a time, however, the whole becomes solid again, and adheres tenaciously to the glass. When pure ammonium amidosulphate is similarly heated in a dry, inactive gas, it becomes coloured, softens, sinters together, vesiculates, gives off ammonia, and becomes a mass like that derived directly from the union of the gases. With very gradual heating, the temporarily liquid product is much less coloured than in the other case, its colour being evidently caused by the presence of red matter dissolved in it, which gives indications of being volatile. This orange-red substance is never formed except in very small quantities. It gives a yellow colour to the aq. soln. of the whole product, which, however, slowly fades. Alcohol, carbon disulphide, and other menstrua dissolve it out from the salts, leaving them white; but the soln. are not pure. The yellow soln. in water or alcohol takes a transient pink colour when mixed with dil. hydrochloric acid, and the alcoholic soln., an indigo-blue colour with concentrated ammonia. The residue left on evaporating the carbon disulphide soln. becomes explosive when heated above 150°, and may then have become nitrogen sulphide, but before being heated it is not this substance.

If ammonium amidosulphinate be heated for some time to 30°–35°, and extracted with 95 per cent. alcohol, E. Divers and M. Ogawa found that a small proportion of a very deliquescent salt is obtained on evaporating the alcoholic soln. The residue has the empirical composition $9NH_3+8SO_2$, and it is probably a mixture. If the alcoholic soln. be cooled, and sat. with ammonia, minute scaly crystals are obtained which, when dried over sulphuric acid, have the composition $(NH_2)_2S_2O_3$—the earlier analyses gave $(NH_3)_2S_2O_3$. E. Divers considers the constitutional formula to be **amidothioimidosulphonic acid,** $NH_2.S.NH.HSO_3$, or



$$HN{<}\begin{matrix}SO_2.O\\S.NH_3\end{matrix}{>}$$

The soln. is freely acid to litmus; when boiled with dil. hydrochloric acid, it gives very little sulphur and no sulphur dioxide; at higher temp., whether dry or in soln., it yields sulphur, sulphur dioxide, and sulphate; and when distilled with alkali-lye it yields no ammonia unless previously heated under press. with hydrochloric acid. This substance has acidic characteristics and furnishes salts:

ammonium amidothioimidosulphonate, $NH_4(N_2H_3S_2O_3)$; **potassium amidothioimidosulphonate,** $K(N_2H_3S_2O_3)$; **barium amidothioimidosulphonate,** $Ba(N_2H_3S_2O_3)_2$; and **lead amidothioimidosulphinate,** $Pb(N_2H_3S_2O_3)_2$.

In addition to the above-mentioned products of the decomposition of ammonium amidosulphinate there are formed as secondary products: sulphamide, amidosulphates, thiosulphates, imidosulphates, sulphur, and sulphates. E. Divers and M. Ogawa also obtained crystals of a substance with the empirical composition and provisional name *pentasulphitotetrammine*, $4NH_3.5SO_2$, by extracting the orange mass of decomposed ammonium amidosulphinate with 95 per cent. alcohol. F. Ephraim and H. Piotrowsky regarded it as $HSO_3.(NH.SO)_3.NH.HSO_3$, but M. Ogawa and S. Aoyama showed that it is more likely to be nothing but impure ammonium trithionate.

C. A. Cameron and J. Macallan[2] reported the formation of **ammonium amidoselenite,** $NH_4(NH_2SeO_2)$—analogous to ammonium amidosulphinite, $NH_4(NH_2SO_2)$—by the action of dry ammonia on a soln. of selenium in absolute alcohol. Minute crystals begin to deposit when the ammonia has been absorbed for some time; and the crystals can be washed with alcohol and dried over sulphuric acid in vacuo. The analysis agreed with the given formula. The deliquescent crystals are said to be hexagonal prisms and pyramids, which at ordinary temp. give off ammonia, forming the acid salt. Ammonium amidoselenite is said to be soluble in warm alcohol; but the soln. slowly deposits the salt in crystals when cooled. 100 parts of alcoholic ammonia at ordinary temp. dissolve 8·33 parts of the salt; more is dissolved at a higher temp. Hydrochloric and nitric acids have only a slight action; conc. sulphuric acid acts vigorously with the development of much heat. The salt is reduced to selenium by sulphur dioxide, or by stannous chloride; barium chloride gives a small precipitate with the warm soln.; and platinic chloride precipitates ammonium chloroplatinate. If the alcoholic soln. of the normal salt be boiled until crystals begin to separate, or if the normal salt be kept for 3 hrs. over sulphuric acid in vacuo, deliquescent crystals of **ammonium hydroamidoselenite,** $(NH_4)H(NH_2SeO_2)$, are formed. 100 parts of alcohol dissolve 7·14 parts of the salt, and it separates in large prisms from the alcoholic soln. When the salt is heated, part volatilizes unchanged, and part is transformed into ammonium selenite. The salt volatilizes in vacuo or in a current of air; it is oxidized by chlorine; and behaves towards sulphur dioxide, stannous chloride, barium chloride, and platinic chloride like the normal salt. Acids, including sulphuric acid, act feebly in the cold.

E. Divers and S. Hada were unable to confirm these results. They found that in the absence of water selenium dioxide is quite indifferent to ammonia in the cold or to its soln. in ether. Although not very soluble in alcohol alone, it dissolves freely in alcoholic ammonia to become, in absence of water, ammonium ethyl selenite, obtainable in the solid state, either by evaporating the alcohol or by precipitating the salt with dry ether. O. Hinsberg has found that an alcoholic soln. of selenium dioxide, free from all water, on evaporation leaves crystals of ethyl hydroselenite, which slowly decomposes again in dry air into alcohol and selenium dioxide, or at once, in contact with water, into alcohol and selenious acid. He also obtained what appeared to be the aniline salt of this compound, in an impure state, by mixing and evaporating soln. of selenium dioxide in alcohol and of aniline in ether, but only in absence of water. Water at once decomposed the salt into alcohol and the acid selenite of aniline. The production of ethyl ammonium selenite acquires interest from the fact that it can be effected only in the entire absence of water, to the action of which the salt is very sensitive. The salt is also of interest because, in mode of formation and in properties, it closely resembles ethyl ammonium sulphite. It is suggested that C. A. Cameron and J. Macallan used ammonia which was not thoroughly dried and that their products were impure ammonium selenites.

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§ 51. Amidosulphonic Acid and its Salts

H. Rose[1] treated ammonium imidosulphonate with lead acetate, and decomposed the lead salt with hydrogen sulphide, and obtained what he called *sulphamic acid*, or *pyrosulphamic acid*. This product was probably impure **amidosulphonic acid,** $NH_2H.SO_3$. E. Berglund, in his memoir *Om imidosulfonsyra*, first definitely described the preparation of the pure acid; J. Sakurai regards this acid as sulphurous acid, $H.SO_2.OH$, with the H-atom replaced by the NH_2-radicle, $NH_2.SO_2.OH$; and just as sulphurous acid, in point of electrical conductivity measurements by W. Ostwald, and K. Barth, behaves like a monobasic acid with ions $H^{\cdot}$ and HSO'_3, so amidosulphonic acid furnishes the ions $H^{\cdot}$ and $NH_2SO'_3$. E. Berglund called it sulphamic acid and also amidosulphonic acid; and E. Divers and T. Haga said the name should be either amine-sulphonic acid, or amidosulphuric acid. E. Berglund obtained this acid by treating barium amidosulphonate with dil. sulphuric acid, and heating the product on a water-bath with the gradual addition of barium hydroxide, still maintaining an acid reaction. When an excess of ammonia and barium hydroxide no longer gives a precipitate of the imidosulphonate, the liquid is sat. with barium hydroxide, the barium sulphate filtered off, and the soln. sat. with carbon dioxide. The clear filtrate is evaporated for the acid. F. Raschig found that a large yield of amidosulphonic acid is obtained by evaporating an aq. soln. of hydroxylamine chloride sat. with sulphur dioxide; and F. Krafft and E. Bourgeois recommended keeping the soln. of hydroxylamine chloride sat. with sulphur dioxide for 2–3 days by means of a slow current of the gas. The acid was purified by crystallization from slightly warm water, but it is easily converted by hot water or by damp air at 130°–140° into ammonium hydrosulphate. E. Divers and T. Haga said that other salts of hydroxylamine or even the base itself can be used in place of the chloride. They preferred the sulphate because the liberated sulphuric acid reduces the solubility if the amidosulphonic acid, whereas hydrochloric acid has very little influence. They also worked with soln. cooled by a freezing mixture. They considered this method to be the most convenient, but it was found to be cheaper to prepare the acid by sulphonating sodium nitrite by means of sulphur dioxide and sodium carbonate, and hydrolyzing the resulting nitrilosulphonate to acid sulphate and amidosulphonate:

Two mols of sodium nitrite, and 3 mols of sodium carbonate are mixed with enough water to make the whole weigh 18 times as much as the sodium nitrite alone. Sulphur dioxide is passed into the soln. until it is acid to litmus. Usually the nitrilosulphonate changes rapidly into the imidosulphonate, but a drop of conc. sulphuric acid hastens the change. There is a marked development of heat, and much sulphur dioxide is evolved owing to the interaction of the acid sulphate and the metasulphite. Warming the mixture for a short time, or allowing it to stand for a few hours, will hasten the hydrolysis of imidosulphonate into amidosulphonate and acid sulphate. The soln. is neutralized by adding a mol of sodium carbonate, and evaporated by boiling or otherwise until it weighs 18 times as much as the sodium nitrite originally taken. The soln. is left overnight in a cool place when nearly all the sodium sulphate will be deposited in crystals. The mother-liquor is drained from the crystals, and the clear soln. of sodium amidosulphonate treated with conc. sulphuric acid weighing 3 to 3½ times that of the sodium nitrite originally employed. The mixture is set aside for a day in a cool place. The crystals of amidosulphonic acid which separate are drained on porous tubes, and washed with a little ice-cold water. The salt can be purified by cooling a soln. of the salt in about 2¾ times its weight of boiling water. The mother-liquors can be worked up by evaporation, and by precipitating the acid with conc. sulphuric acid or alcohol. A yield of 75 per cent. is readily obtained.

A soln. of the acid is also obtained by treating, say, barium amidosulphonate (*q.v.*) with the calculated quantity of dil. sulphuric acid. E. Divers and T. Haga found that the acid is formed by reducing hydroxylamine sulphonic acid, $HO.N(HSO_3)_2$, in acid soln. by a copper-zinc couple, by sodium amalgam, or by zinc and sulphuric acid. E. Divers and T. Haga found that potassium nitrososulphate forms some amidosulphonate when reduced by sodium amalgam. E. Berglund observed that a mixture of sulphur trioxide with an excess of ammonia sometimes yields a little ammonium amidosulphonate along with imidosulphonate; W. Traube found that sulphamide is decomposed by boiling alkali-lye into amidosulphonate and ammonia. F. Krafft and E. Bourgeois, and P. Eitner obtained acetyl acetamidosulphonate by the action of fuming sulphuric acid on acetonitrile, and this readily hydrolyzes into acetamide and amidosulphonic acid. M. Schmidt obtained amidosulphonic acid by treating acetoxime with sulphurous acid. E. Berglund showed that methyl sulphate and ammonia do not form methyl amidosulphonate, but rather primary, secondary, and tertiary sulphates and ammonium sulphate. W. Traube and E. Brehmer found that the salts of fluosulphonic acid possess the remarkable property of exchanging the fluorine atom for an amine-group when treated with an aq. soln. of the requisite base; under these conditions, a portion of the fluosulphonic acid, greater or less according to the strength of the base, is hydrolyzed to hydrofluoric and sulphuric acids, which represent the sole by-products of the change and which can be removed readily by chalk or barium hydroxide. A number of alkyl amidosulphonates were prepared in this manner.

Amidosulphonic acid is described by E. Berglund as being colourless and odourless, and having a sharp, purely acid taste; it crystallizes from its aq. soln. better than most of its salts. The crystals are rhombic plates which, according to A. Fock, have the axial ratios $a:b:c=0{\cdot}9048:1:1{\cdot}1487$, and are isomorphous with the potassium salt. E. Divers and T. Haga found the sp. gr. in ether to be 2·03 at 12°. M. Schmidt said that the m.p. is near 200°; and E. Divers and T. Haga found the apparent m.p. to be near 205°, but added that the acid has no real m.p. because in the act of melting it decomposes. The evolution of vapour at the m.p. is but slight in dry air, but is greatly affected by the presence of moisture in the acid or in the surrounding air. E. Berglund said that when amidosulphonic acid is rapidly heated in the absence of moisture, it is decomposed, forming sulphur dioxide, nitrogen, water, sulphuric acid, and, added E. Divers and T. Haga, ammonia. Below the temp. at which these changes occur, near 205°, the acid undergoes an intramolecular change. In a closed space protected from air, the acid sustains no loss in half an hour when heated to 220°, and only about 1 per cent. when heated to 260°; just below 260° small bubbles very slowly form in the liquid, but become reabsorbed if the temp. is lowered; they consist, almost certainly, of ammonia. There is much expansion in the act of melting, the unmelted particles sinking freely in the melted part; on cooling, the liquid forms a vitreous mass, which contracts so much as partly to detach itself from the glass, even cracking this when very thin. The vitreous product is brittle, exceedingly deliquescent, and very soluble in water. If kept dry, it remains quite transparent, and shows no tendency to crystallize even after the lapse of several days. The vitreous mass has the same ultimate composition as the acid, and when dissolved in water it furnishes ammonium hydrosulphate owing to its interaction with the solvents. It is therefore inferred that nearly half the amidosulphonic acid is converted into a sulphate. When the vitreous mass is dissolved in alkali-lye, sulphuric acid and ammonia are the chief products, though the proportion of the former is less than before, but the amount of the latter is about the same, and in excess of that required for ammonium sulphate; imidosulphate is also present in the alkaline soln. Some ammonia is present in the vitreous mass as ammonium imidosulphonate which hydrolyzes into sulphate and amidosulphonic acid more readily in water than in alkali-lye. It is therefore inferred that ammonium sulphate and imidosulphonate are produced by heat without any escape of gas. This is only possible if the sulphate and imidosulphonate exist as their unknown pyrosalts. Analyses agree with the presence of mol. proportions of *ammonium pyrosulphate*, $(NH_4)_2S_2O_7$, and *ammonium imidosulphate*, $(NH_4)NS_2O_5$; thus, $4NH_2.HSO_3=(NH_4)_2S_2O_7+(NH_4)NS_2O_5$. When the acid is heated above 260°, dense white vapours of sulphur trioxide, sulphur dioxide, and nitrogen appear; as the temp. rises decomposition proceeds more rapidly, and the vapours become more transparent. The pyro-salts formed below 260° are supposed to decompose as represented by $5(NH_4)_2S_2O_7+5(NH_4)NS_2O_5=6NH_4HSO_4+3HN(NH_4SO_3)_2+2N_2+NH_3+6SO_2+2SO_3$. The decomposition at still higher temp. causes the residue to become richer in water, and poorer in ammonia and imidosulphate until at last ammonium hydrosulphate alone remains. When heated in ordinary damp air at 100°, amidosulphonic acid slowly fixes water by hydrolysis, and the surface of the crystals becomes sticky. F. Krafft and E. Bourgeois said that this change proceeds freely at 130°–140°, while E. Berglund found that the change does not occur below 190°; but in the latter case, moisture was not concerned in the reaction.

D. Takahashi found that subcutaneous injections of sodium amidosulphonate into a frog, and intravenous injections in a dog produced no injurious symptoms, indicating that the amidosulphonates have no direct toxic action on animals. O. Loew observed no injurious effects on infusoria, rotatoria, and copepoda; but amidosulphonic acid has a decidedly noxious action on phanerogams; while mould fungi and bacteria can utilize amidosulphonic acid as a source of nitrogen. Amidosulphonic acid is stable in air, and not deliquescent when cold, but generally retains about one per cent. of moisture either hygroscopically or as ammonium hydrosulphate. According to E. Berglund, the acid is very soluble in water; but it is less soluble than any of its salts excepting the silver and basic mercury salts. E. Divers and T. Haga found that 100 parts of water at 0° dissolve 20 parts of amidosulphonic acid, and at 70°, 40 parts. Hot water has some chemical action on the salt so that an accurate determination of the solubility is not practicable. No other solvent has been found. The addition of sulphurous acid greatly depresses the solubility; sodium hydrosulphate acts similarly. Nitric and acetic acids act similarly but to a less degree; while fuming hydrochloric acid does not reduce the solubility. A. Hantzsch and B. C. Stuer found the mol. electrical conductivity, μ, of soln. with a mol of the acid in v litres of water at 0°; and J. Sakurai, at 25°, to be:

	0°				25°			
v .	75·7	151·4	302·8	1211·2	32	128	512	∞
μ .	216·9	229·1	239·7	246·8	295·8	341·9	361·9	374·0

Amidosulphonic acid has about the same strength as iodic acid, and is a much stronger acid than sulphurous acid. The percentage degree of ionization is 79·09 for the 32 v soln., 91·42 for the 128 v soln., 96·79 for the 512 v soln.; and 97·99 for the 1024 v soln. E. Berglund found that the acid is fairly stable in cold aq. soln., and the presence of neither dil. hydrochloric acid, nor a mixture of hydrochloric acid and barium chloride, affects its stability in the cold; but a mixture of hydrochloric acid and barium chloride may be boiled for an hour before barium sulphate is precipitated. He said that the acid in aq. soln. can be boiled for an hour without decomposition, though it is broken down by continued boiling. Hydrochlorous acid hastens the hydrolysis of the acid. F. Raschig also emphasized the stability of aq. soln. of the acid, and F. Krafft and E. Bourgeois emphasized the instability of the acid in warm aq. soln. According to E. Divers and T. Haga, an aq. soln. of the acid can be boiled for a moment, or kept at 100° for a very few minutes, without showing any sign of sulphuric acid with the barium chloride test, but when kept for 2 hrs. at 45°, the soln. gives a turbidity with barium chloride in 20 secs. Platinum black acts slowly on an aq. soln. of amidosulphonic acid exposed to air, producing sulphuric acid by simple hydrolysis. E. Berglund found that amidosulphonic acid is not decomposed by a boiling soln. of potassium hydroxide, while F. Raschig said that the alkali-lye made the acid less stable; E. Divers and T. Haga found alkali-lye to be inactive. The potassium salt can be evaporated on the water-bath without noticeable change; and W. Traube prepared an alkali amidosulphonate by boiling sulphamide with alkali-lye. F. Raschig stated that the presence of acids accelerates the hydrolysis, but E. Divers and T. Haga found that the hydrolysis of a boiling soln. in the presence of hydrochloric acid is not completed in a few hours; but 3–4 hrs.' heating at 150° completes the hydrolysis. Crystals of amidosulphonic acid may be kept for months over conc. sulphuric acid without change, and when heated, the acid dissolves and decomposes as it does when heated alone. Amidosulphonic acid is decomposed with effervescence due to the escape of nitrous oxide, when treated with a mixture of conc. sulphuric acid and a nitrate or nitric acid, even at ordinary temp.—*vide* imidosulphonates. According to M. Gurewitsch, amidosulphuryl chloride is produced by the action of thionyl chloride on amidosulphonic acid: $NH_2.SO_2.OH+SOCl_2=SO_2+HCl+NH_2.SO_2.Cl$, and it is formed as a complex with phosphorus trichloride by the action of phosphorus pentachloride on amidosulphonic acid: $NH_2.SO_2.OH+2PCl_5=POCl_3+HCl+Cl_2+NH_2.SO_2Cl.PCl_3$ —*vide infra.* The reaction of amidosulphonic acid with sulphuric and nitric acids was observed by J. Thiele and A. Lachmann, but no nitramide was obtained. E. Divers and T. Haga found that amidosulphonic acid is oxidized by hot or cold nitric acid, and by chlorine or bromine; while E. Berglund found that it is oxidized by a mixture of nitric acid or potassium chlorate and hydrochloric acid. E. Divers and T. Haga found that amidosulphonic acid is not acted on by soln. of chromic acid, potassium permanganate, or ferric chloride; but it is slowly oxidized at a boiling heat by silver oxide and alkali-lye and the glass containing vessel is silvered. Sulphates are not oxidized by silver oxide in alkaline soln. so that the reaction is taken to be: $NH_2.KSO_3+Ag_2O=AgKSO_3+Ag+N+H_2O$. F. Krafft and E. Bourgeois showed that amidosulphonic acid combines with alcohol, forming ammonium ethyl sulphonate; and C. Paal and F. Kretschmer, that with aniline, ammonium phenylamidosulphonate is formed. E. Divers and T. Haga found that amidosulphonic acid retards the precipitation of sulphates and sulphites by barium chloride; it also prevents the precipitation of silver and mercuric salts by alkalies. The aminic character of the acid is emphasized in the latter reaction. E. Berglund said that amidosulphonic acid dissolves zinc, and iron; and E. Divers and T. Haga, that when acted on by sodium it furnishes hydrogen and the sodium salt. It does not decompose alkali chlorides or nitrates when mixed with the salt in a damp state or in a soln.; but if mixed dry and heated, the acid itself is decomposed. F. Raschig said that the acid crystallizes unchanged from a soln. in hydrochloroplatinic acid. L. Herboth recommended amidosulphonic acid as a standard for titrimetric work because of the ease of preparation, its keeping qualities in air, and the accuracy of titrations made with it when dimethylaminedoazobenzene, methyl-red, phenolphthalein, or rosolic acid is used as indicator.

As indicated above, amidosulphonic acid is monobasic, forming a series of salts, the **amidosulphonates** or *amidosulphites.* The methods of preparation employed by E. Berglund, and F. Raschig can be much simplified because the isolation of the acid is now usually easier than the preparation of the salts. E. Berglund made **ammonium amidosulphonate,** $NH_4.SO_3NH_2$, by double decomposition with, say ammonium sulphate, and barium amidosulphonate. It forms large plates which melt at 125°. The ammonium salt is liable to hydrolysis if not quite dry; when heated to 160°, it decomposes: $2(NH_4)NH_2SO_3=NH_3+NH(NH_4SO_3)_2$, but the yield of imidosulphonate is small. After heating to 170°, the cold residue is a gum-like mass. E. Divers and T. Haga treated hydroxylamine sulphate with an eq. of barium amidosulphonate and obtained a soln. of **hydroxylamine amidosulphonate,** $NH_2.HSO_3.NH_2OH$, as a viscous, hygroscopic liquid. A. P. Sabanéeff succeeded in crystallizing the liquid ; and he also obtained the salt by passing sulphur dioxide into an excess of a methyl-alcoholic soln. of hydroxylamine. The dry salt is fairly stable ; the crystals are isomeric with those of hydrazine sulphate ; and the aq. soln. decomposes on a water-bath. A. P. Sabanéeff also prepared **hydrazine amidosulphonate,** $N_2H_4.HSO_3.NH_2$, from neutral hydrazine sulphate and barium amidosulphonate. No acid salt could be made. The soln. concentrated in a desiccator crystallizes with great difficulty. The salt is easily soluble in water. F. Ephraim and E. Lasocky were not successful in the nitration of amidosulphonic acid because of its insolubility in both nitric and sulphuric acids ; but by treating the silver salt with methyl iodide, they obtained microscopic rhombohedra of **methyl amidosulphonate,** $NH_2.SO_2.OCH_3$. The crystals begin to fuse at 170° and have a m.p. about 198° (decomp.). The ester cannot be nitrated, but by treatment with liquid ammonia, sulphamide can be obtained from it.

E. Berglund prepared acicular, deliquescent crystals of **lithium amidosulphonate,** NH_2SO_3Li, by double decomposition. The salt decomposes at 160°–170° into ammonia and imidosulphonate. It is insoluble in alcohol. E. Divers and T. Haga observed that amidosulphonic acid forms a complex salt with sodium sulphate—**sodium sulphatoamidosulphonate,** $6NH_2(HSO_3).5Na_2SO_4.15H_2O$—which appears in short, thick, deliquescent prisms. E. Berglund obtained **sodium amidosulphonate,** $NH_2.NaSO_3$, in bundles of striated needles by double decomposition. E. Divers and T. Haga obtained it by the action of sodium carbonate on the acid. E. Berglund said that the salt is easily soluble in water ; insoluble in alcohol ; and at 160°–170° forms ammonia and the imidosulphonate. E. Berglund made **potassium amidosulphonate,** by double decomposition ; and F. Raschig, by hydrolyzing potassium imidosulphonate, or nitrilosulphonate with boiling water, removing the free sulphuric acid by calcium carbonate, and evaporating the filtrate. The less soluble potassium sulphate crystallizes out first. According to A. Fock, the rhombic plates have the axial ratios $a:b:c=0{\cdot}9944:1:0{\cdot}7097$. E. Berglund, and E. Divers and T. Haga showed that at 160°–170°, ammonia and imidosulphonate are formed. The salt is easily soluble in water, and it readily forms supersaturated soln. It is insoluble in alcohol. H. Stamm found that the salt is more soluble in water if ammonia be present. W. Traube and E. von Drathen found that eq. proportions of soln. of potassium amidosulphonate and hypochlorous acid react in the cold to form **potassium chloroamidosulphonate,** $NHCl.SO_3K$, which may be isolated by evaporating the mixture to a small bulk, in a high vacuum, at as low a temp. as possible and precipitating with alcohol. The salt forms limpid, hygroscopic crystals, and is comparatively stable. When warmed with mineral acids, hydrolysis takes place according to the equation: $NHCl.SO_3H+H_2O=NH_2Cl+H_2SO_4$. The corresponding **potassium bromoamidosulphonate** is very similar. Similar salts may be prepared by the interaction of free aminosulphonic acid and metallic hypochlorites. Alkylaminosulphonates apparently give very unstable products, for evolution of gas is noticed as soon as hypochlorous acid is added. There are indications that a double amount of hypochlorous acid produces less stable **dichloroamidosulphonates.**

E. Berglund prepared **copper amidosulphonate,** $Cu(NH_2SO_3)_2.2H_2O$, by double decomposition, and A. Callegari by the action of the acid on the carbonate. The evaporation of the soln. in vacuo over sulphuric acid, or precipitation with alcohol gives a pale blue, microcrystalline powder which is fairly soluble in water ; and loses its water at a high temp. with decomposition. C. Paal and F. Kretschmer also made the copper salt. E. Berglund obtained **silver amidosulphonate,** NH_2SO_3Ag, from barium amidosulphonate, and a soln. of silver sulphate in boiling water. The silver salt was also described by P. Eitner, and C. Paal and F. Kretschmer. E. Divers and T. Haga said that the silver salt is best made directly from the acid ; it cannot be prepared from the potassium salt and silver nitrate since the most conc. soln. of these salts, mixed in equimolar proportions, give no crystalline precipitate, and when the mixture is evaporated to dryness mixed crystals of silver and potassium nitrates, and amidosulphates. E. Berglund said that the silver salt crystallizes best of all the amidosulphonate results. It forms bundles of striated prisms, and the crystals are as hard and brittle as glass. The salt blackens very slowly. Silver amidosulphonate is also least soluble since 100 parts of water at 19° dissolve 6·7 parts of salt. The aq. soln. is neutral. F. Ephraim and M. Gurewitsch found that when a soln. of amidosulphonic acid is neutralized with ammonia, and the calculated quantity of silver nitrate added to form the silver salt, no precipitate forms until the liquid has been evaporated to a syrupy consistence. It then solidifies suddenly to a radiating crystalline mass, which, after crystallization from water, gives rhombohedral crystals of **ammonium silver amidosulphonate,** $NH_2.SO_3Ag.NH_2.SO_3NH_4$. According to E. Divers and T. Haga, when potassium hydroxide is added to a soln. of silver amidosulphonate, an ochre-yellow colloidal precipitate is deposited. This compound has one of the amido-hydrogen atoms replaced by silver so as to form **potassium argentamidosulphonate,** $AgHN.SO_3K$. If the potassium hydroxide be in excess, the supernatant liquor is golden yellow; if much water is added, the colour of precipitate and soln. becomes brown and the precipitate dissolves. Both the brown and yellow soln. give brown precipitates when heated, or when mixed with an excess of potassium hydroxide, silver nitrate, or potassium amidosulphonate. The yellow soln. gelatinizes and becomes colourless on standing. The brown substance in soln. and the precipitate are said to be essentially silver oxide. The yellow compound is not blackened by light, is soluble without colour in potassium amidosulphonate, is slowly converted to a whitish, pulverulent precipitate by digestion with silver nitrate soln., and into a white flocculent precipitate by excess of potassium hydroxide. Its soln. in a minimum of potassium amidosulphonate silvers glass at a boiling heat, so does a soln. of potassium amidosulphonate, silver nitrate, and potassium hydroxide. A soln. of silver amidosulphonate does not sensibly dissolve silver oxide. A soln. containing silver nitrate and its eq. of potassium amidosulphonate behaves towards potassium hydroxide like silver amidosulphonate. If the silver nitrate is present in excess, and the soln. not too dil., precipitation of the amidosulphonic compound precedes that of silver oxide, but if the proportion of potassium amidosulphonate is as 2 mols. to 1 of the silver nitrate, potassium hydroxide causes no precipitate in soln. of moderate conc., that is to say, amidosulphonic acid prevents the precipitation of silver oxide by alkalies. A soln. of 2 mols. of potassium amidosulphonate, 2 mols. of potassium hydroxide, and 1 mol. of silver nitrate dries up in the desiccator to a white, homogeneous mass of minute, silky fibres, soluble in water again without change. Alcohol extracts from it no notable quantity of potassium hydroxide. The white fibrous salt is a complex of potassium argentamidosulphonate, and *potassium potassamidosulphonate*, $KNH.SO_3K$, and potassium nitrate. K. A. Hofmann and co-workers found that the *hydrate*, $NHAg.SO_3K,H_2O$, is obtained, by the action of silver nitrate on an alkaline soln. of potassium amidosulphonate, in the form of silky, colourless, flat needles, which are strongly double-refracting, with parallel extinction. The stability of the combination of silver with the amide-nitrogen is of the same order as in the silver ammines. The salt is soluble in ammonia, the soln. giving a precipitate of silver with formaldehyde, and a beautiful silver mirror with tetraformaltrisazine. **Potassium gold amidosulphonate,** $Au_2(N.SO_3K)_3$, is prepared from gold chloride and an alkaline soln. of potassium amidosulphonate; it forms small, yellow, transparent, granular crystals, and detonates on heating. The ammoniacal soln. gives a gold mirror with formaldehyde or tetraformaltrisazine. The aq. soln. catalyzes hydrogen peroxide, colloidal gold being formed.

E. Berglund prepared thin plates of **calcium amidosulphonate,** $Ca(NH_2SO_3)_2.4H_2O$, which were very soluble in water; also prismatic crystals of **strontium amidosulphonate,** $Sr(NH_2SO_3)_2.4H_2O$, more soluble than the barium salt; and acicular and prismatic crystals of **barium amidosulphonate,** $Ba(NH_2SO_3)_2$. The aq. soln. can be kept a long time without change. The solid does not decompose at 200°. E. Divers and T. Haga represented the thermal decomposition by $3Ba(NH_2SO_3)_2 = 3BaSO_4 + HN(SO_3NH_4)_2 + NH_3 + NS + N$. W. Traube and E. von Drathen prepared **barium chloroamidosulphonate,** $(NHCl.SO_3)_2Ba$, by the method indicated for the potassium salt. No *magnesium amidosulphonate* has been reported. E. Berglund prepared a radiating mass of crystals of **zinc amidosulphonate,** $Zn(NH_2SO_3)_2.4H_2O$, by double decomposition, etc.; and rhombic plates of **cadmium amidosulphonate,** $Cd(NH_2SO_3)_2.5H_2O$, in a similar way. The latter salt is very soluble in water.

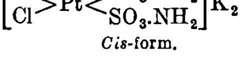
E. Divers and T. Haga said that **mercurous amidosulphonate** cannot exist (in aq. soln.), for, when a soln. of mercurous nitrate is treated with the acid, metallic mercury and **mercuric oxyamidosulphonate,** $Hg(NH_2.SO_3HgO)_2.2H_2O$, is formed. According to E. Berglund, when silver amidosulphonate is mixed with mercuric chloride, a mixed precipitate of silver chloride and mercuric oxyamidosulphate is set free, and amidosulphonic acid passes into soln. According to E. Berglund, and E. Divers and T. Haga, normal **mercuric amidosulphonate** cannot be prepared. The oxyamidosulphonate is formed when mercuric oxide and moist amidosulphonic acid are ground together—any excess of mercuric oxide can be removed by dil. nitric acid, and any excess of amidosulphonic acid passes into soln. When potassium hydroxide is added to a mixed soln. of mercuric chloride and potassium amidosulphonate a precipitate of the basic salt is produced when the mercuric chloride is not in excess. Amidosulphonic acid can precipitate all the mercury from a soln. of mercuric nitrate leaving only nitric acid in soln.; and the acid is precipitated completely on adding a slight excess of mercuric salt. Mercuric oxyamidosulphonate is best obtained by mixing a dil. soln. of the acid with a conc. soln. of mercuric nitrate in a minimum quantity of nitric acid. The snow-white, voluminous, finely divided precipitate is troublesome to wash, and to dry. It is very stable and can be washed with hot water. The air-dried salt is dihydrated, but the water is all expelled at 115°. The basic salt is soluble in cold conc. nitric acid, in hydrochloric acid, and in an excess of a soln. of potassium hydroxide; if the alkali be not in excess, the basic salt is partially decomposed, forming yellow mercuric oxide. Mercuric chloride in the presence of an excess of amidosulphonic acid is not precipitated by an excess of potassium hydroxide; and the addition of more mercuric chloride, or of a little acid, causes the white basic salt to be precipitated, but not mercuric oxide. It is supposed that in alkaline soln., **potassium mercurammonium hydroxysulphonate,** $Hg_3N_2(HO)_2(KSO_3)_2$, is present; and like other mercurammonium salts it does not yield up its ammonia when treated with alkalies; it is resolved into its amine and mercuric bromide by a sat. soln. of ammonium bromide: $Hg_3N_2(HSO_3)_2(OH)_2 + 12NH_4Br = 3HgBr_2(NH_4Br)_2 + 2NH_2SO_3NH_4 + 4NH_3 + 2H_2O$; and it is converted into white precipitate when treated with a dil. soln. of ammonium chloride—at the same time, a soln. of mercury ammonium chloride and ammonium amidosulphonate is formed without the liberation of ammonia. K. A. Hofmann and co-workers prepared **potassium mercuric amidosulphonate,** $NHg.SO_3K$, by neutralizing 40 grms. of amidosulphonic acid with 10 per cent. potassium hydroxide, adding a further 40 c.c. of the alkali, and then digesting on the water-bath with the freshly precipitated mercuric oxide prepared from 100 grms. of mercuric chloride. On concentrating the soln. the required salt separates, after cooling, in the form of thin, lancet-shaped flakes, which are strongly doubly-refracting. The salt crystallizes only very slowly from soln., even when inoculated with a crystal, the various phenomena observed indicating that the crystals are probably polymerides of the mols. in soln.; the same holds for the other salts to be described. The interaction of the salt with a number of reagents is described, the results all pointing to the fact that it is a true derivative of amidosulphonic acid. If carbon dioxide is passed for some time through the mother-liquors obtained in the preparation of the above salt, an amorphous white precipitate of **potassium mercuric hydro-amidosulphonate,** $KH(SO_3N)_2Hg(Hg.OH)_2,H_2O$, is obtained. Complete saturation with carbon dioxide under press. gives finally the free acid, $(HSO_3.N)_2Hg.OH)_2$. **Sodium mercuric amidosulphonate,** $NHg.SO_3Na$, is prepared similarly to the potassium salt; it forms radiating clusters, or often felted masses, of slender, colourless needles. It differs from the potassium salt in that it is soluble in water on heating, whereas the addition of alkali is necessary to dissolve readily the former salt.

E. Berglund reported **thallium amidosulphonate,** $TlNH_2SO_3$, to be formed in prismatic crystals by the process of double decomposition. The crystals are isomorphous with those of potassium. He also made short needles of **lead amidosulphonate,** $Pb(NH_2SO_3)_2.H_2O$, by the double decomposition process. The salt is very soluble in water, but not deliquescent. C. Paal and F. Kretschmer also made this salt. E. Berglund obtained a soluble **uranyl amidosulphonate ;** and he prepared rose-red crystals of **manganese amidosulphonate,** $Mn(NH_2SO_3)_2.3H_2O$, in an analogous way. These salts are very soluble in water.

E. Divers and T. Haga made **ferrous amidosulphonate,** $Fe(NH_2SO_3)_2.5H_2O$, by dissolving iron wire in amidosulphonic acid with the exclusion of air. The acid is best kept sat. The bluish-green soln. is evaporated in vacuo. The soln. like that of most other amidosulphonates is very liable to supersaturation. The crystals appear in the form of a cake of radiating prisms. The salt is deliquescent, and is not precipitated by alcohol. They also obtained a soln. of **ferric amidosulphonate** by dissolving ferric hydroxide in amidosulphonic acid. The bright brown soln. dries to an opaque, amorphous, brittle mass. It is soluble in water, but not at all deliquescent. It has the full astringent taste of the inorganic salts, not that of the citrate or tartrate.

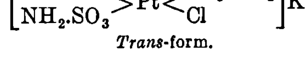
E. Berglund prepared **cobalt amidosulphonate,** $Co(NH_2SO_3)_2.3H_2O$, and nickel amidosulphonate, $Ni(NH_2SO_3)_2.3H_2O$, by the action of barium amidosulphonate on the corresponding sulphates. F. Ephraim and W. Flügel prepared **cobalt hexamminoamidosulphonate,** $[Co(NH_3)_6]NH_2SO_3)_2$, with a solubility at 20° of 0·2470*N*-; **cobalt aquopentamminoamidosulphonate,** $[Co(NH_3)_5(H_2O)](NH_2SO_3)_3$, with a solubility 0·723*N*- ; **cobalt diaquotetramminoamidosulphonate,** $[Co(NH_3)_4(H_2O)_2](NH_2SO_3)_3$, with a solubility of 1·002*N*- ;. **cobalt nitritopentamminoamidosulphonate,** $[Co(NH_3)_5(NO_2)](NH_2SO_3)_2$, with a solubility of 0·5076*N*-; **cobalt cis-dinitritotetramminoamidosulphonate,** $[Co(NH_3)_4(NO_2)_2](NH_2SO_3)$, with a solubility of 0·158*N*-; **cobalt trans-dinitritotetramminoamidosulphonate,** $[Co(NH_3)_4(NO_2)_2](NH_2SO_3)$, with a solubility of 0·123*N*- ; and **cobalt carbonatopentamminoamidosulphonate,** $[Co(NH_3)_5(CO_3)](NH_2SO_3)$, which is very freely soluble.

H. Kirmreuther prepared two **potassium dichlorodiamidosulphonatoplatinites** by the action of potassium chloroplatinite on amidosulphonic acid. The α-salt, $[Cl_2Pt(NH_2.SO_3)_2]K_2,2H_2O$, is yellow and readily soluble, whilst the β-salt, $[Cl_2Pt(NH_2.SO_3)_2]K_2$, is almost colourless and more difficultly soluble. Both salts contain only the potassium in an ionogenic condition, and both are neutral, so that they cannot be structural isomerides in accordance with the formulæ: $[Cl_2Pt(SO_3.NH_2)_2]K_2$ and $[Cl_2Pt(NH.SO_3H)_2]K_2$. Both salts dissolve in potassium hydroxide, giving an intense golden-yellow soln. containing a tetra-potassium salt; they must, therefore, be derived from the second of the above formulæ, that is, they are platosimines. Acids re-precipitate the salts from the soln. in potassium hydroxide. These salts are considered to be stereoisomerides, similar to the dichloroplatosamines, and from their analogy with already known isomerides of platinum, the α-salt is characterized as the *cis*-form, and the β-salt as the *trans*-form,



$$\left[{}^{Cl}_{Cl}\!>\!Pt\!<\!{}^{SO_3.NH_2}_{SO_3.NH_2}\right]K_2$$

Cis-form.



$$\left[{}^{\quad\ \ Cl}_{NH_2.SO_3}\!>\!Pt\!<\!{}^{SO_3.NH_2}_{Cl}\right]K_2$$

Trans-form.

H. Kirmreuther also prepared **potassium cis-dichlorodiamidosulphonatoplatinite** by the interaction of a mol of potassium platinochloride and two mols of amidosulphonic acid in cold aq. soln. After keeping for 24 hrs. the soln. deposits tabular, golden-yellow crystals, which are weakly pleochroic; they belong probably to the rhombic system, and are soluble to the extent of one part in 38 parts of water at 21°. One mol of water is lost at 90° and two mols at 130°. Barium chloride and hydrochloric acid give no precipitate, even on warming, proving that the sulphamic acid residue is in the inner complex sphere. Pyridine replaces the amidosulphonic acid from the residue, giving *cis*-dichloro-pyridine platinum. **Potassium trans-dichlorodiamidosulphonatoplatinite** is obtained when more than two mols of amidosulphonic acid react with 1 mol of potassium chloroplatinate, the reaction being best carried out on the water-bath. After heating for two to three hours, the soln., on cooling, deposits a mass of almost colourless, felted needles, which dissolve in water to the extent of one part in 342 parts at 21°. The reactions of this salt are similar to those of the *cis*-isomeride, except that pyridine gives the *trans*-dichlorodipyridineplatinite. **Potassium trans-dibromodiamidosulphonatoplatinite,** $[Br_2Pt(SO_3NH_2)_2)K_2$, and **potassium trans-diiododiamidosulphonatodiplatinite,** $[I_2Pt(SO_3NH_2)_2]K_2$, were obtained from the dichloro-compound by interaction with potassium bromide and iodide respectively. The former gives bright orange-yellow prisms, whilst the latter forms reddish-brown prisms. L. Ramberg and S. Kallenberg treated platinous hydroxide with an aq. soln. of amidosulphonic acid and obtained **ammonium tetramidosulphonatoplatinite,** $(NH_4)_2[Pt(NH_2SO_3)_4].6H_2O$; and when treated with sodium chloroplatinite it furnishes **sodium tetramidosulphonatoplatinite,** and this, with potassium nitrate, yields **potassium tetramidosulphonatoplatinite,** $K_2(Pt(NH_2SO_3)_4].2H_2O$; and the same salt was obtained by the action of silver amidosulphonate on the potassium *cis*-dichlorodiamidosulphonatoplatinite of H. Kirmreuther.

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§ 52. Imidosulphinic Acid and its Salts

E. Divers and M. Ogawa[1] observed that when ammonium amidosulphinate is gently heated, it decomposes: $2NH_2SO_2NH_4=NH_3+NH(SO_2NH_4)_2$, thus furnishing the ammonium salt of **imidosulphinic acid,** or *imidosulphurous acid*, $NH(HSO_2)_2$. The acid has not been isolated. They prepared **ammonium imidosulphinite,** $NH(NH_4SO_2)_2$, or $3NH_3.2SO_2$, by keeping ammonium amidosulphinate for several hours at 35° protected from moisture.

In order to prepare the ammonium imidosulphite, ammonia in excess and sulphur dioxide are led into a closed flask, fitted with a thermometer and an exit-tube dipping in mercury. To absorb the heat caused by the combination of the gases, the flask is held in a bath of brine and crushed ice, which is more effective when the flask contains some ether and is kept in motion, because then the salt does not stick to the walls of the flask as a waxy, badly-conducting coating. The rate of flow of the gases is to be regulated by the operator's ability to prevent the temp. in the flask from rising much above 10°. The inside of the apparatus, the gases, and the ether are all to be dried before use. The mottled, orange-coloured mass of waxy consistence sticks to the walls of the containing vessel, and must be protected from air. Though only sparingly soluble, it can be nearly all removed by protracted digestion with successive portions of 95 per cent. alcohol until the residue is colourless, and then with 90 per cent. alcohol at about 50°. As the soln. cools, it deposits the almost pure imidosulphinite. The impure salt deposited from other extracts is washed with ammoniacal alcohol to dissolve out foreign salts, then crystallizing the residue from its soln. in 90 per cent. alcohol. The crystals are dried on a porous tile, while protected from air, and finally in a desiccator over potassium hydroxide.

Ammonium imidosulphinite forms minute, acicular crystals which are moderately deliquescent, and when freshly prepared are neutral to litmus. It has a mild, unpleasant, sulphurous taste. When heated slowly in a tube, it soon begins to decompose into volatile substances, and a residue of sulphur, ammonium sulphate, and the imidosulphonate, $NH(NH_4SO_3)_2$. The sublimates begin to appear at about 80°, and consist of ammonium pyrosulphite, $(NH_4)_2S_2O_5$, and unchanged imidosulphinite. No fusion occurs even at 150°. The salt is freely soluble in water, but is slowly decomposed, forming thiosulphate, and amidosulphonate. The change begins at once, and it is continued in the presence of hydrochloric acid, which, when hot, slowly hastens its completion: $2NH(NH_4SO_2)_2+2HCl=2NH_4SO_3NH_2+2NH_4Cl+SO_2+S$, in which the sulphur and sulphur dioxide represent undecomposed thiosulphuric acid. The salt is insoluble in alcohol, and in this respect differs from ammonium amidosulphinate. When boiled with an aq. soln. of potassium hydroxide, ammonium imidosulphinite yields two-thirds of its nitrogen as ammonia.

When an alcoholic soln. of potassium hydroxide is added to a soln. of ammonium imidosulphinite in 70 per cent. alcohol, until the liquid colours red litmus permanently blue in air, **potassium imidosulphinite,** $NH(KSO_2)_2$, soon separates in minute, micaceous crystals which adhere firmly to the glass walls of the containing vessel. After washing with absolute alcohol, the salt is still alkaline to litmus, possibly owing to the presence of the tripotassium salt as impurity. Potassium imidosulphinite is very soluble in water, and it gives the imidosulphinite reactions characteristic of that salt. When the orange mass of decomposed ammonium imidosulphinite is mixed with baryta-water so as to leave undecomposed some of the contained imidosulphinite, the concentration of the filtered soln. in a desiccator furnishes small, micaceous crystals of **ammonium barium imidosulphinite,** $Ba(SO_2.NH.SO_2.NH_4)_2$.

F. Ephraim and H. Piotrowsky obtained a red compound by the action of an excess of ammonia on sulphur dioxide. It has the same composition, but twice the mol. wt. of ammonium amidosulphite; and it is considered to be **triammonium imidodisulphinite,** $NH_4.N:(SO_2.NH_4)_2$. It furnishes **trisilver imidodisulphinite,** $Ag.N:(SO_2.Ag)_2$, which is also red in colour. It is not very stable, and gradually loses nitrogen. It was also found that when thionyl chloride is added drop by drop to liquid ammonia, the liquid assumes the same intense red colour as that possessed by the product formed from sulphur dioxide and excess of ammonia. On evaporation, a cinnabar-red residue is left, contaminated with ammonium chloride and other products. On digestion with absolute alcohol at —5°, a deep red soln. is obtained, which, on evaporation in a vacuum, gives a residue consisting of amorphous, red flakes, easily soluble in water, and mixed with a small quantity of stable, golden-yellow crystals (not enough to analyze completely), which are only slightly soluble in water. The red flakes consist of the above-mentioned triammonium imidodisulphinite, which gradually decomposes with loss of colour. The freshly prepared aq. soln., when added to ammoniacal silver nitrate, gives a purple-red precipitate of the trisilver imidodisulphinite. The reactions are symbolized;

$2SOCl_2+7NH_3=4NH_4Cl+HN:(SO.NH_2)_2$. This diamide is readily hydrolyzed by water, giving $NH(SO_2.NH_4)_2$, from which the silver salt is obtained by precipitation. The soln. of the diamide in liquid ammonia is red, probably containing the compound $NH_4N:(SO.NH_2)_2$; there is presumably enough water in the liquid ammonia to convert this amide into the above-mentioned triammonium imidodisulphinite on evaporation.

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§ 53. Imidosulphonic Acid and its Salts

The more important memoirs on this subject are E. Berglund's[1] *Om Imidosulfonsyra*, and E. Divers and T. Haga's *Imidosulphates*. V. A. Jacquelain first prepared an aq. soln. of amidosulphonic acid, or imidosulphuric acid. His method, also employed by E. Berglund, and E. Divers and T. Haga, consists in treating the lead salt of the acid suspended in water with hydrogen sulphide. The filtered soln. when concentrated in vacuo contained very little sulphuric acid, showing that very little hydrolysis had occurred. The conc. soln. is unstable, and the acid is only known in aq. soln. E. Frémy attempted to obtain it by adding hydrofluosilicic acid to the potassium salt, but said the product decomposed immediately into sulphuric and sulphurous acids, and ammonia—but there is probably some misunderstanding here—*vide infra.* The aq. soln. of the acid prepared by E. Frémy was called *sulphamidinic acid*, and that by A. Claus and S. Koch was called *disulphammonic acid*. The aq. soln. is very unstable, and readily forms sulphuric and amidosulphonic acids. Aq. soln. of the salts decompose in a similar way, so that, as shown by F. Raschig, a feebly acid soln. of barium chloride, precipitates only half the sulphur as barium sulphate; and potassium hydroxide was shown by E. Berglund not to set the ammonia at liberty. F. Raschig found that if the acid of an imidosulphonate is heated with conc. hydrochloric acid in a sealed tube at 150°, the compound is completely decomposed. There are two series of **imidodisulphonates**; in one; all three hydrogen atoms of the acid are replaced by the basic radicle—these are sometimes called *basic imidosulphonates;* and in the other, only two of the hydrogen atoms are displaced—these are called the *neutral imidosulphonates.* The normal salts are usually more soluble than the basic salts. The unstable **imidomonosulphuric acid,** $NH:N.HSO_3$, or rather **potassium imidomonosulphonate,** $NH.N.KSO_3$, was stated by F. Raschig to be formed by the action of potassium permanganate on potassium hydrazinomonosulphonate—*vide infra*, diazomonosulphonic acid.

H. Rose found that when dry ammonia is conducted into a flask coated inside with sulphur trioxide, two products are formed—one is hard and vitreous; and the other is local and flocculent. V. A. Jacquelain obtained the flocculent substances by mixing the vapour of sulphur trioxide with an excess of dry ammonia. H. Rose said that both these substances when dissolved in water gave a soln. which yielded crystals of the same substance which he called *parasulfatammon*, and which is now known to be *diammonium imidosulphonate*, $NH(SO_2NH_4)_2$, *i.e.* $3NH_3.2SO_2$. Sometimes the vitreous product is acidic, which H. Rose attributed to the imperfect action of ammonia, but which E. Divers and T. Haga showed to be a consequence of hydrolysis. H. Rose thought that the crystals of parasulphatammon have the same composition as the flocculent matter, $2NH_3.SO_2$, which he called *sulfatammon.* V. A. Jacquelain showed that this is a mistake, and M. Woronin found that H. Rose's analyses of sulfatammon, $2NH_3.SO_3$, was correct, and that sulfatammon and parasulfatammon were really different salts of the same acid. E. Berglund then claimed that since *parasulfatammon* is diammonium imidosulphonate, *sulfatammon* must be *triammonium imidodisulphonate,* $N(NH_4)(NH_4SO_3)_2$, *i.e.* $4NH_3.2SO_3$. E. Divers and T. Haga showed that E. Berglund's view is correct; and confirmed M. Woronin's observation that the evaporation of the soln. of the triammonium salt furnishes the diammonium salt.

H. Rose prepared **triammonium imidodisulphonate,** $N(NH_4)(NH_4SO_3)_2$, by the action of ammonia on sulphur trioxide, and V. A. Jacquelain passed the dry sulphur trioxide in a flask filled with gaseous ammonia so as to keep the ammonia always in excess. The flocculent product was then fused in a current of ammonia until, on cooling, the mass began to solidify. The white crystals are stable in air. E. Divers and T. Haga exposed the finely divided and dry diammonium salt to an atm. of dry ammonia, and found that the absorption of the gas is attended by a considerable swelling of the powder, and the formation of the triammonium salt. According to H. Rose, this substance is a white, anhydrous, amorphous powder having a bitter taste resembling that of ordinary ammonium sulphate, and a neutral reaction. It is stable in air. E. Divers and T. Haga said that the product loses only about half per cent. of its weight when kept in a desiccator for 3 days over sulphuric acid. It seems to lose ammonia only in a damp atm.; and it lost 5·4 per cent. of its weight when heated in a current of well-dried air for $1\frac{3}{4}$ hrs. at 100°–120°, but the compound was then still losing ammonia. H. Rose said that when this compound is heated in air it gives off sulphur dioxide, ammonia, and ammonium sulphite, fuses to a clear liquid, and solidifies to a mass of ammonium hydrosulphate; and when heated in hydrogen, ammonia and ammonium sulphite are evolved, and the residue contains ammonium hydrosulphite and sulphate. The aq. soln. does not change on keeping, but when evaporated, crystals of the diammonium salt are deposited; 100 parts of water dissolve 11·1 parts of the salt at ordinary temp. If the soln. be mixed with barium chloride or nitrate, only part of the contained sulphur is precipitated as sulphate, and even after a prolonged boiling with nitric or hydrochloric acid, only about half the total sulphur is precipitated as sulphate. The whole of the sulphuric acid can be recovered as sulphate only by evaporating the soln. to dryness with barium chloride, and strongly igniting the residue. Strontium chloride gives a scanty precipitate with the aq. soln. after the lapse of about a week; and with calcium chloride the soln. was clear at the end of a week. In both cases, the boiling soln. gives a turbidity with these salts. When the aq. soln. is digested with calcium hydroxide until all the ammonia is evolved, calcium sulphate remains as a residue; lead acetate added to the aq. soln. gradually produces a turbidity, but even with a boiling soln., the sulphuric acid is only partially precipitated. Hot sulphuric acid dissolves the salt slowly, without the evolution of sulphur dioxide; the salt is decomposed again as the soln. cools. A soln. of the salt gives a precipitate with aluminium sulphate, tartaric acid, and racemic acid only after a long interval of time, and in less amount than would be obtained with an aq. soln. of ammonium sulphate. An alcoholic soln. of hydrochloroplatinic acid precipitates rather more than half the contained ammonia. The salt does not dissolve in alcohol, and does not suffer any change when digested with that liquid.

E. Divers and T. Haga prepared **monohydrated triammonium imidodisulphonate,** $N(NH_4)(NH_4SO_3)_2.H_2O$, by the union of ammonia with diammonium imidosulphonate in the presence of water. The ammonia must be in excess or the salt will be decomposed. Conc. aq. ammonia precipitates this salt from a sat. soln. of the diammonium salt, or from a sat. soln. of the sodium salt, but in that case the precipitate is contaminated with the double sodium ammonium salt. Ammonia gas acts similarly and more effectively. The crystalline powder can be recrystallized by cooling a hot conc. soln. of ammonia in a closed vessel. The crystals resemble those of the potassium salt. The clear, lustrous crystals gradually effloresce and become opaque and damp; and in a dry ammoniacal atm. over solid potassium hydroxide, the crystals slowly become opaque and anhydrous. When heated, the salt partly fuses and passes into the diammonium salt with the loss of both ammonia and water ; at the same time there is some hydrolysis into the sulphate. When the salt is dissolved in water, it decomposes incompletely into the diammonium salt and ammonia ; on evaporation, crystals of the diammonium salt are formed.

As just indicated, H. Rose showed that **diammonium imidodisulphonate,** $NH(NH_4SO_3)_2$, is produced by evaporating the aq. soln. of the triammonium salt; H. Rose, V. A. Jacquelain, and M. Woronin also found parasulfatammon to be a by-product in the preparation of sulfatammon from sulphur trioxide and ammonia. E. Berglund, and A. Mente made it by the action of ammonia on chlorosulphonic acid ; A. Mente, by the action of ammonia on sulphuryl or pyrosulphuryl chloride ; E. Frémy, by the action of nitrous gas on an ice-cold soln. of ammonium sulphite and hydrolyzing the product ; E. Berglund, by heating ammonium amidosulphonate to 160°; E. Divers and T. Haga, by treating either of the lead hydroxyimidosulphonates with ammonium carbonate; by treating barium imidosulphonate fused with dil. sulphuric acid, and then with ammonium sulphate until all the barium is precipitated; and finally, by stirring triargentic imidosulphonate with an eq. soln. of ammonium bromide. The filtered, aq. soln. of the salt is evaporated, while kept alkaline with a drop of conc. ammonia to prevent hydrolysis ; and allowed to crystallize.

The clear, colourless, lustrous, monoclinic crystals were shown by L. Münzing to have the axial ratios $a:b:c=1\cdot6443:1:0\cdot9672$, and $\beta=92°\ 45'$. They are isomorphous with the corresponding potassium salt. A. Mente gave 1·965 for the sp. gr. H. Rose said that the salt does not absorb moisture from the air. The salt is rather more stable in water than the triammonium salt, and the soln. is neutral, but V. A. Jacquelain found that the soln. reddens blue litmus even when free from sulphuric acid; this, said E. Berglund, is a result of hydrolysis. H. Rose said that the product obtained by heating this salt differs but little from those obtained by heating ammonium sulphate except that no water is present—ammonia and sulphur dioxide are evolved, and if the temp. is not too high ammonium hydrosulphate remains as a residue; ammonium sulphite and sulphate are present in the sublimate. V. A. Jacquelain reported that the salt can be fused without decomposition, and can be kept in a fused condition in an atm. of dry ammonia, without change ; but, according to E. Divers and T. Haga, in vacuo, diammonium amidosulphonate suffers no change until very near 357°, when it melts, effervesces, and boils. A little sublimate may appear at about 190°, most of the vapours from the molten salt consist of unchanged imidosulphonate, but there is a slow decomposition: $6NH(NH_4SO_3)_2=2N_2+14NH_3+6H_2O+6SO_2+6SO_3$; and there is also formed the pyrosulphite, $(NH_4)_2S_2O_5$, and the pyrosulphate, $(NH_4)_2S_2O_7$. Any ammonia evolved without admixed nitrogen is due to the action of moisture on the somewhat deliquescent salt: $NH(NH_4SO_3)_2+H_2O=H_2N.NH_4SO_3+NH_4HSO_4=NH_3+(NH_4)_2S_2O_7$. According to H. Rose, the evaporation of the aq. soln. in air gives the unchanged salt as well as some ammonium sulphate and sulphuric acid. The aq. soln. gives no precipitate with salts of barium, strontium, calcium, or lead even after standing a long time ; but if the soln. has become acidic, or if boiled with barium chloride, a little barium sulphate may be precipitated; barium chloride and hydrochloric acid together give a precipitate after the lapse of about 12 hrs. The aq. soln. in nine parts of water gives no precipitate with tartaric acid after standing several days ; with racemic acid it gives a scantier precipitate than is obtained with the triammonium salt; and it behaves like the triammonium salt with aluminium sulphate, and hydrochloroplatinic acid. No precipitation occurs when the aq. soln. is treated with manganese, copper, or silver nitrate.

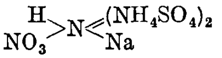
E. Berglund prepared **trisodium imidodisulphonate,** $NaN(NaSO_3)_2.12H_2O$, by adding the potassium salt to a boiling soln. of sodium chloride and hydroxide ; the salt separates in thin plates on cooling the soln., and it can be recrystallized from water. E. Divers and T. Haga followed the process for the preparation of the disodium salt so far as to separate a crop of sodium sulphate crystals, the soln. is then diluted with water, sodium hydroxide added in slight excess, and the liquid is cooled. The trisodium salt begins to separate soon after the addition of the sodium hydroxide. The salt can be purified by recrystallization. The crystals, said E. Berglund, are large and micaceous; while E. Divers and T. Haga described them as thin, overlapping, hexagonal plates. The salt is stable, but the crystals effloresce in dry air, and have a mild alkaline taste. The salt is sparingly soluble in cold water, but is very soluble in hot water—at 27·5°, 100 parts of water dissolve 18·5 parts of salt. The soln. is readily supersaturated ; it is alkaline to litmus and to phenolphthalein ; and it has no action on a soln. of iodine. The salt is precipitated by alcohol from its aq. soln. without decomposition, and it can be repeatedly crystallized from its aq. soln. without the loss of alkali. The crystals melt when heated, and their water may be driven off, causing a decomposition of the salt. In vacuo over sulphuric acid, the crystals lose 11 mols. of water, and accordingly E. Divers and T. Haga write the formula $NaN(NaSO_3)_2.H_2O+11H_2O$. The salt loses more water when heated, but retains some at 160°—possibly through hydrolysis. If heated until decomposition begins, the salt yields a little water and ammonia, but more when heated in air than in vacuo. When the dried salt is heated strongly in an open tube, it melts and effervesces, yielding nitrogen, sulphur dioxide, and a sublimate of sulphur ; the saline mass at a red-heat is *hepar sulphuris*. If heated in vacuo, no sulphur dioxide is formed, so that that gas if present is produced by the action of air on sulphur. Just below the softening temp. of soda-lime-glass, the gas given off is nitrogen, some of the sulphur remains in the fused mass and is partly elemental, and partly thiosulphate ; a trace of ammonium sulphite sublimes; but the main reaction is represented: $2NaN(NaSO_3)_2=N_2+S+3Na_2SO_4$. Acids dissolve the trisodium salt, and if the right proportion of acid is added, the disodium salt is formed. Conc. sulphuric acid, not in excess, dissolves the crystals with a fall of temp., but if more than enough to form the disodium salt is present, heat is developed, and the neutralized soln. furnishes crystals of sodium sulphate and the disodium salt. Carbon dioxide decomposes a conc. soln. precipitating sodium hydrocarbonate ; conc. aq. ammonia precipitates the dodecahydrated trisodium salt free from ammonia; ammonium salts react by double decomposition, forming the triammonium salt which is partly decomposed by water giving off ammonia ; and potassium salts, say the nitrate, added to conc. soln. produce no change, but when neutralized with an acid, the sodium salt is deposited. Unlike the disodium salt, soln. of the trisodium salt give precipitates with metal salt soln.—in some cases hydroxides are formed, and with silver, mercury, lead, calcium, and barium nitrates yield imidosulphonates. There is no visible action with mercuric chloride ; and mercuric oxide dissolves to a limited extent in soln. of the trisodium salt.

E. Divers and T. Haga prepared **heptahydrated pentasodium ammonium imidosulphonate,** $Na_5NH_4N_2(SO_3)_4.7H_2O$, in small prisms, by cooling to 0°, a mixed soln. of the disodium salt and conc. ammonia. The dry salt is stable. If conc. ammonia be added to a soln. of the trisodium salt containing the eq. of 3 mols. of sodium nitrate, a crystalline precipitate of the **hemipentahydrate,** $Na_5NH_4N_2(SO_3)_4.2\frac{1}{2}H_2O$, is formed. It loses water and ammonia when heated.

E. Berglund noted that some **dilithium imidosulphonate,** $NH(LiSO_3)_2$, is formed when lithium amidosulphonate (*q.v.*) is heated to 160°–170°. E. Divers and T. Haga prepared **disodium imidosulphonate,** $NH(NaSO_3)_2.2H_2O$, by mixing 2 mols of sodium nitrate and 3 mols of sodium carbonate with twice their weight of water, and passing sulphur dioxide into the soln. The containing vessel is kept cool with cold water. When the liquid is almost neutral to lacmoid paper, the flow of gas is slackened, and stopped as soon as the liquid reddens the test-paper permanently. Neglecting intermediate stages, the main reaction at this stage may be symbolized: $2NaNO_2+3Na_2CO_3+8SO_2=2N(NaSO_3)_3+Na_2S_2O_5+3CO_2$. The excess of pyrosulphite is necessary to convert all the nitrite into the nitrilic salt; and its presence helps to preserve the imidosulphonate subsequently formed. The soln. also contains but very little sulphate. The soln. then becomes warm and gives off sulphur dioxide, owing to a partial hydrolysis of the nitrilic salt: $2N(NaSO_3)_3+Na_2S_2O_5+H_2O=2NH(NaSO_3)_2+2Na_2SO_4+2SO_2$, so that the soln. contains nothing but imidosulphonate, sulphate, and sulphur dioxide. The sulphur dioxide is removed by passing a current of air through the liquid for about 30 minutes; and sodium carbonate is added to render the liquid slightly alkaline. The liquid is concentrated by evaporation on the water-bath, and cooled to 0° so as to crystallize out the sulphate; a second evaporation and cooling may be necessary to eliminate more sulphate. Another evaporation and cooling to ordinary temp. causes the separation of dihydrated disodium imidosulphonate in well-formed crystals. The yield is about 80 per cent., and the main losses are due to the mixture of sodium sulphate and imidosulphonate in the mother-liquor. The salt can be purified by recrystallization from warm water made slightly alkaline to prevent hydrolysis. Instead of using sodium carbonate, fresh sodium sulphite or pyrosulphite can be used. The disodium salt can be made from the trisodium salt—the latter is the more stable salt. The trisodium salt is treated with dil. sulphuric acid until neutral to litmus, and the mixture kept for some hours at 0°. The clear liquor, on evaporation, yields good crystals of the dihydrated disodium salt.

Disodium imidosulphonate furnishes large rhombic prisms. It is very soluble in water; it has a slight acidic reaction, and is devoid of sulphurous taste. The crystals do not effloresce in air; but in air dried by conc. sulphuric acid, they slowly become opaque, and lose their water. They can be kept in a dry atm. indefinitely, but they are liable to hydrolyze into an acidic mixture of sulphate and amidosulphonate. The aq. soln. of the salt can be moderately heated for a short time, but is liable to hydrolysis. The crystals suffer some hydrolysis at 100°. The salt also decomposes when it is dehydrated. It decomposes when heated in a manner analogous to the dipotassium salt (*vide infra*). The disodium salt is more fusible than the potassium salt. The disodium salt does not give a precipitate with many of the common metal salts; but in moderately conc. soln., it gives a precipitate of the dipotassium salt, with potassium salts; of the trisodium salt, with sodium hydroxide; of the barium sodium salt, with barium hydroxide; and of the sodium ammonium salt, with ammonia: $5NH(NaSO_3)_2+5NH_3=2N_5(NH_4)N_2(SO_3)_4+NH_4N(NH_4SO_3)_2$; but if sodium nitrate, or chloride is added before the ammonia the reaction is: $NH(NaSO_3)_2+NH_3+NaNO_3=NH_4NO_3+NaN(NaSO_3)_2$. Basic lead acetate gives a copious precipitate, normal lead acetate a scanty precipitate, but lead nitrate no precipitate. The latter salt favours hydrolysis so that a little lead sulphate is soon precipitated. Both mercury nitrates give precipitates; precipitated mercuric oxide gives mercury disodium imidosulphonate; silver hydroxide forms the silver disodium salt; and cupric hydroxide has no visible action when evaporated on the water-bath; with sodium carbonate or acetate, some trisodium salt is formed, and carbon dioxide or acetic acid vapour escapes. In the latter case, a strong acid vapour rises from a highly alkaline liquid.

If a mixture of a soln. of the trisodium salt with a slight excess over an eq. proportion of ammonium nitrate be evaporated, ammonia escapes, and the acid soln. is neutralized with ammonia from time to time; water is also added if necessary to dissolve any crystals. During the cooling of the hot soln., crystals of **sodium ammonium nitratoimidodisulphonate**, $NH(NH_4SO_3)_2.NaNO_3$, are formed in small, flat, thick prisms, which are anhydrous, and stable in air. The salt cannot be washed with water, or recrystallized from water without hydrolysis. If too little ammonium nitrate is used the complex salt is contaminated with some disodium imidosulphonate. The constitution is represented with quinquevalent nitrogen:



$$\begin{matrix}H\\NO_3\end{matrix}>N<\begin{matrix}(NH_4SO_4)_2\\Na\end{matrix}$$

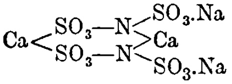
E. Berglund prepared **tripotassium imidodisulphonate**, $NK(KSO_3)_2.H_2O$, by dissolving the potassium salt in a soln. of potassium hydroxide, evaporating, and cooling. The salt can be purified by recrystallization from the smallest proportion of hot water. F. Raschig used this process. The well-formed, triclinic crystals were found by A. Fock to have the axial ratios $a:b:c=0.9796:1:0.8415$. The water of crystallization is given off at about 100°. E. Berglund found the salt can be heated to 200° without change, and it is also stable in aq. soln. The salt is not oxidized by permanganate, and with the heavy metals it forms sparingly soluble potassiferous precipitates.

E. Berglund obtained **dipotassium imidosulphonate,** $NH(KSO_3)_2$, by heating potassium amidosulphonate to 160°–170°. E. Divers and T. Haga worked at 350°, when the salt melts and decomposes: $2H_2N(KSO_3)=NH(KSO_3)_2+NH_3$. E. Frémy, A. Claus, and F. Raschig hydrolyzed potassium nitrilosulphonate with a little dil. sulphuric acid; and A. Claus and S. Koch observed that the dipotassium salt is formed by crystallization from soln. of potassium nitrilosulphonate in boiling water, or acidulated water. F. Raschig said that the yield is poor. M. Woronin made the dipotassium salt by decomposing the barium salt with potassium sulphate. E. Berglund, and E. Frémy added potassium chloride to a soln. of the diammonium salt, and recrystallized the dipotassium salt from luke-warm water, or dil. aq. ammonia; and E. Divers and T. Haga obtained the salt in a similar manner by double decomposition of the disodium salt with potassium salt. Dipotassium imidosulphonate furnishes small six-sided plates (E. Frémy); six-sided pyramids resembling augite (A. Claus and S. Koch); or long needles and granular aggregates (F. Raschig). L. Münzing said that the crystals belong to the monoclinic system, and have the axial ratios $a:b:c=1.6555:1:0.9573$, and $\beta=86°\ 31'$; while P. Friedlander said the crystals are rhombic with the hexagonal habit in consequence of trilling. E. Frémy said that the salt does not change in moist air; and, according to E. Divers and T. Haga, and A. Claus and S. Koch, not at 140°–150° in moist air. E. Divers and T. Haga found that at 170°–180°, the dipotassium salt slowly fixes water and hydrolyzes so that the imidosulphonate loses its crystalline lustre, cakes together, and become acid. If the salt be thoroughly dried, and in a dry atmosphere below the softening temp. of soda-lime-glass, no notable change occurs. If the air is not dried, the salt begins to increase in weight owing to the action of absorbed moisture. E. Frémy, and A. Claus and S. Koch reported that at about 200°, potassium sulphate, sulphur dioxide, ammonia, and a coloured sublimate are formed; but, according to E. Divers and T. Haga, they did not report the formation of a white sublimate as well, and also the evolution of nitrogen, which shows that the salt is not an addition compound of ammonia. In vacuo, the salt yields a slight sublimate between 360° and 440°; and at the temp. of decomposition the salt melts and boils: $3NH(KSO_3)_2=N_2+NH_3+3SO_2+3K_2SO_4$. The sublimates are a product of the union of sulphur dioxide and ammonia. There was no evidence of the intermediate formation of nitrilosulphonate: $3HN(KSO_3)_2=NH_3+2N(KSO_3)_3$. E. Berglund said that the dipotassium salt is less soluble than the other normal imidosulphonates, and E. Frémy added that 100 parts of water dissolve 1·56 parts of salt at 23°. Boiling water, said F. Raschig, transforms the salt into the amidosulphonate, and E. Frémy, and A. Claus and S. Koch showed that with acidulated water, sulphur dioxide, ammonium sulphate, and potassium sulphate are formed. E. Berglund found that the dipotassium salt dissolves in a soln. of potassium hydroxide, forming the more soluble tripotassium salt which, according to F. Raschig, can be precipitated by carbon dioxide. A. Claus said that sulphur dioxide does not decompose the cold aq. soln. E. Frémy, and A. Claus and S. Koch observed the slight action exercised by sulphuric and nitric acids on the dipotassium salt. E. Divers and T. Haga said that very little sulphuric acid is obtained by extracting the cold mass with ether or alcohol; and they add that there is no evidence of a reaction: $NH(KSO_3)_2+2H_2SO_4=2KHSO_4+NH(HSO_3)_2$. E. Divers and T. Haga studied the action of sulphuric acid; and they observed that a dry mixture of the dipotassium salt and potassium hydrosulphate may be fused without appreciable chemical action, but at 420°–450°, the imidosulphonate is decomposed the same as it is when heated alone—moisture must be excluded.

E. Frémy observed no apparent decomposition of the dipotassium salt by treatment with cold conc. nitric acid. A. Claus and S. Koch found that the dil. soln. gives a precipitate with lead acetate; while the hot conc. soln. gives a basic lead acetate; and E. Frémy obtained a crystalline double salt when the aq. soln. is treated with barium chloride. E. Divers and T. Haga observed that the dipotassium salt gives many of the reactions observed with the disodium salt (*q.v.*). E. Divers and T. Haga found that the sparingly soluble dipotassium salt is hardly affected by digestion with a cold dil. soln. of sodium nitrate; and if dissolved therein, it crystallizes out again almost unchanged. If a soln. containing 3 mols of sodium nitrate be allowed to stand in contact with a mol of powdered dipotassium imidosulphonate for some days, a granular mass of **potassium sodium dinitratoimidodisulphonate,** $NH(KSO_3)_2.NaNO_3.KNO_3$, is formed; it is decomposed by water. Neither the two potassium imidosulphonates nor the two sodium imidosulphonates form double salts. Disodium imidosulphonate and potassium nitrate suffer double decomposition, but the reaction is reversible. F. Raschig obtained **potassium chloroimidodisulphonate,** $NCl(SO_3K)_2$, in colourless, anhydrous crystals, when a hot soln. of sodium hypochlorite and potassium imidodisulphonate, $NH(SO_3K)_2$, is allowed to cool slowly to the ordinary temp. The substance is unstable and decomposes into nitrogen trichloride and potassium nitrilosulphonate, $N(SO_3K)_3$.

According to E. Divers and T. Haga, when silver nitrate is gradually added to a soln. of tripotassium or trisodium imidosulphonate, there is first formed a white precipitate which redissolves, there is then a separation of a felted mass of white crystals, which redissolve, with the subsequent separation of a granular mass of minute crystals. Silver nitrate and trisodium imidosulphonate yield three compounds in which 1, 2, and 3 atoms of, say, sodium are replaced by silver. If a limited amount of the trisodium salt be added to silver nitrate, a white precipitate of **trisilver imidodisulphonate,** $AgN(AgSO_3)_2$, is formed. E. Berglund first prepared this salt. E. Divers and T. Haga found that the trisilver salt is very slightly soluble in water, but is not decomposed by that liquid in washing, although after long washing it yields a turbid filtrate of the colloidal salt. The voluminous precipitate forms white, chalk-like masses when dried; the dried mass retains about 0·55 per cent. of water even after a protracted heating at 110°. At a high temp. the salt decomposes with or without fusion, giving, in an open tube, a little ammonia, and a slight sublimate, then sulphur dioxide, nitrogen, silver, and silver sulphide and sulphate. In vacuo, there is scarcely any sublimate, and no change occurs until the temp. attains 440°, when nitrogen and sulphur dioxide are evolved, and the residue blackens without fusion, and consists of silver sulphide and sulphate, and silver. The reactions are probably: $4AgN(AgSO_3)_2=2N_2+2SO_2+5Ag_2SO_4+Ag_2S$; and $4AgN(AgSO_3)_2=2N_2+4SO_2+4Ag_2SO_4+4Ag$, the latter being more pronounced the higher the temp. The granular precipitate indicated above is **disilver sodium imidodisulphonate,** $NaN(AgSO_3)_2$, and it is best made by adding the trisodium salt to a little less than two-thirds its eq. of silver nitrate. The faint, buff-coloured, granular mass is quickly washed, and dried on a porous tile. The salt consists of microcrystalline, hexagonal plates which act on polarized light. The salt is sparingly soluble in water, and is slightly decomposed by it, forming some silver hydroxide. The retention of water and the behaviour of heat resemble closely the results with the trisilver salt except that sodium sulphate forms one of the products of decomposition. The interlacing fibrous crystals, indicated above, consist of **silver disodium imidodisulphonate,** $AgN(NaSO_3)_2$; and the salt is prepared by adding the trisodium salt to less than one-third its eq. of silver nitrate, and the mixture agitated at once so as to redissolve the white silver salt first precipitated before the fibrous crystals begin to form. The salt is dried by press. in a calico filter, and between porous tiles. This is the most soluble of the three silver salts, but it is even then only sparingly so; the salt is gradually decomposed by water, forming silver hydroxide, disodium imidosulphonate, and the trisodium and sodium disilver salts. It is therefore difficult to obtain the salt pure. It retains water, and behaves when heated like the preceding salt. E. Berglund said that when silver nitrate is added to an excess of a soln. of the trisodium salt, the precipitate contains more silver than corresponds with the trisilver salt. This is due to the hydrolysis of the silver disodium salt in dil. soln. with which E. Berglund worked.

E. Berglund reported **tricalcium imidodisulphonate,** $Ca\{NCa(SO_3)_2\}_2.8H_2O$, to be formed by mixing soln. of the trisodium salt and calcium chloride. E. Divers and T. Haga showed that the product of this reaction is always sodium calcium imidosulphonate—*vide infra.* If the triammonium salt is used then no sparingly soluble salt is formed. The normal salt, tricalcium imidodisulphonate, is produced, when the trisilver salt is treated with an eq. amount of a soln. of calcium chloride, and evaporating the clear soln. for crystallization. E. Divers and T. Haga also made this salt by the less satisfactory process in which a soln. of diammonium imidosulphonate is treated with the calculated amount of calcium hydroxide, and the ammonia all expelled by two or three evaporations of the soln. to dryness. The salt is only sparingly soluble in water, from which it crystallizes in rectangular prisms and plates which are stable in air. They also made **calcium hydroimidodisulphonate,** $NHCa(SO_3)_2.3H_2O$, by decomposing the trisilver salt with two-thirds an eq. of calcium chloride, and a little less than one-third an eq. of hydrochloric acid; and also by the less satisfactory method of mixing the diammonium salt with the calculated proportion of calcium hydroxide, and repeatedly evaporating the soln. to expel all the ammonia. The evaporation of the aq. soln. furnishes a mass of radiating prisms, which, when dried on porous tiles, are permanent in air. When the calculated quantity of calcium hydroxide is dissolved in a soln. of the diammonium salt, a liquid is obtained which furnishes crystals of what are considered to be **ammonium calcium imidodisulphonate,** possibly $NH_4NCa(SO_3)_2.nH_2O$. They also made **sodium calcium imidodisulphonate,** $NaNCa(SO_3)_2.3H_2O$, by adding a soln. of calcium chloride to an eq. amount of trisodium imidosulphonate; on cooling, the double salt separates in prismatic crystals which can be recrystallized from water. The salt is sparingly soluble in cold water, and absorbs carbon dioxide from the atm. Remembering the uncertainty in the relative positions of sodium and calcium in the mol., the graphic formula can be written:

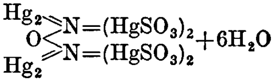


$$Ca<\begin{array}{l}SO_3{-}N<SO_3.Na\\ \qquad\qquad >Ca\\ SO_3{-}N<SO_3.Na\end{array}$$

According to E. Divers and T. Haga, E. Berglund seems to have made a mistake with respect to the strontium imidosulphonate similar to that he made with the normal calcium salt. They obtained **tristrontium imidodisulphonate,** $Sr\{NSr(SO_3)_2\}_2.12H_2O$, by dissolving the strontium sodium salt in dil. hydrochloric acid and filtering the soln. into a warm conc. soln. of strontium hydroxide, repeating the operation twice or until all the sodium is removed. The soln. deposits thin scaly crystals which can be dried on a porous tile. When freshly prepared the salt is a dodecahydrate, but after two weeks' exposure, it forms a heptahydrate. The strontium salt is more soluble than the barium salt, and is fairly soluble in hot water. When an ammoniacal soln. of the diammonium salt is mixed with a slight excess of a conc. soln. of strontium chloride, mixed with an excess of conc. aq. ammonia, and the soln. allowed to evaporate in a desiccator over potassium carbonate, a white powder is formed which is the normal tristrontium salt with a slight quantity of ammonia in addition, and not *ammonium strontium imidosulphonate.* If the normal strontium salt is boiled with water, a basic salt can be formed, **tristrontium trihydroxyimidodisulphonate,** $(SrOH)N\{(SrOH)SO_2\}_2.5H_2O$. E. Berglund made **strontium hydroimidodisulphonate,** $NHSr(SO_3)_2.nH_2O$, by a method analogous to that employed for the calcium salt, but found the product so soluble, and so difficult to crystallize, that he did not examine it further. E. Divers and T. Haga prepared **sodium strontium imidodisulphonate,** $NaNSr(SO_3)_2.3H_2O$, by mixing moderately conc. soln. of strontium chloride and the trisodium salt in the molar proportions 3 : 2. The precipitate first formed dissolves on shaking, and the soln. deposits small prismatic crystals of the double salt which is sparingly soluble in water, and which resembles the corresponding calcium salt. E. Berglund mixed soln. of strontium chloride and the tripotassium salt, and obtained a granular mass of **potassium strontium imidodisulphonate**; his analyses calculated by E. Divers and T. Haga agree with $Sr_{12}K_8H(NS_2O_6)_{11}.3H_2O$. The salt was probably impure.

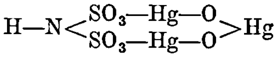
The reports of M. Woronin, and V. A. Jacquelain on barium imidosulphonates refer in both cases to double salts. E. Berglund first made **tribarium imidodisulphonate,** $Ba\{NBa(SO_3)_2\}_2.5H_2O$. It was also prepared by E. Divers and T. Haga as a voluminous, coherent precipitate when the trisodium salt is gradually added to an excess of a soln. of barium chloride. The washed precipitate is dried on a porous tile in thin layers exposed to air. It is difficult to remove adherent water. The water is lost very slowly at 115°. Under the microscope, the white powder appears to consist of long, slender, interlacing needles. The salt is only slightly soluble in water, just enough to make the water give a slight opalescence with sulphuric acid. The soln. is alkaline to litmus, and is decomposed by alkali carbonates. The salt is soluble in dil. nitric acid, and reprecipitated from the soln. by barium hydroxide. This property enables the product to be purified from sodium salts. V. A. Jacquelain, E. Berglund, and E. Divers and T. Haga prepared **barium hydroimidodisulphonate,** $NHBa(SO_3)_2.H_2O$, by adding cautiously to the tribarium salt a little less than one-third the eq. of sulphuric acid; and evaporating the clear soln. in a desiccator. The minute, rhombic crystals are moderately soluble in water. The soln. is acid to litmus, but neutral to methyl orange. The salt is stable in a desiccator in a dry atm., but it soon hydrolyzes in ordinary air at 140°. If rapidly heated it decomposes suddenly, giving a cloud of barium sulphate. When treated with ammonia, the insoluble tribarium salt and ammonium imidosulphonate are formed. M. Woronin prepared this salt, but he assigned to it a mol of water more, and called it *barium sulphamate*, $Ba(H_2NSO_3)_2$, which is the same as $BaNH(SO_3)_2.H_2O$, when the water is regarded as constitutional. V. A. Jacquelain, M. Woronin, and E. Berglund made impure **ammonium barium imidodisulphonate**; and E. Divers and T. Haga added that the gelatinous precipitate obtained by treating the diammonium salt with barium hydroxide soon becomes granular, and consists of granular crystals interspersed with slender needles of the tribarium salt in insignificant amounts. Analyses agreed with the formula $Ba_5(NH_4)_2N_4(SO_3)_8.8H_2O$. The product may be a solid soln. of $Ba_3N_2(SO_3)_4$ and $NH_4NBa(SO_3)_2$ with water of crystallization. E. Frémy, E. Berglund, and E. Divers and T. Haga prepared **potassium barium imidodisulphonate** by the action of baryta-water on the dipotassium salt. E. Berglund, and E. Divers and T. Haga made **sodium barium imidodisulphonate,** $Ba_{11}Na_8N_{10}(SO_3)_{20}.13H_2O$, which may be a solid soln. of $NaNBa(SO_3)_2$ and $Ba_3N_2(SO_3)_4$ with water of crystallization. This salt is formed as a crystalline precipitate by slowly adding a dil. soln. of the barium chloride to an excess of the trisodium salt. The salt is alkaline to litmus; very sparingly soluble in water; readily soluble in nitric or hydrochloric acid; and decomposed incompletely by ammonium carbonate. It does not lose appreciable amounts of water below 120°, but when heated quickly to a higher temp., it is dissipated in a cloud of barium sulphate.

Normal *mercurous imidosulphonate* has not been isolated. The only mercurous imidosulphate known is the basic salt prepared by E. Divers and T. Haga by adding disodium imidosulphonate to an excess of powdered mercurous nitrate which has been stirred up with water until all has passed into soln. except a little basic nitrate: $8HgNO_3+H_2O+2NH(NaSO_3)_2=\{Hg_4N(SO_3)_2\}_2O+4NaNO_3+4HNO_3$. The resulting **mercurous oxyimidosulphonate,** $\{Hg_4N(SO_3)_2\}_2O.6H_2O$, or



is white and flocculent. It loses very little weight at 100°–120°, and part of that loss is due to the volatilization of mercury, for the salt becomes grey. At a higher temp. it becomes black, and then white again; at a red-heat, the salt fuses and effervesces, evolving nitrogen, but no sulphur dioxide. The dark red liquid is mainly a mixture of mercury sulphates. This salt is more soluble in dil. nitric acid than the basic mercuric salt; conc. hydrochloric acid, even in the cold. causes the formation of some mercury and mercuric chloride, and on heating the change is complete owing to the production of amidosulphonic acid. A soln. of sodium chloride becomes alkaline owing to the formation of trisodium imidosulphonate; a cold conc. soln. of potassium iodide dissolves it, leaving half its mercury as metal; and trisodium imidosulphonate converts it into mercury and sparingly soluble disodium mercuric imidosulphonate, hence the trisodium salt is not used in the preparation of the basic mercurous salt.

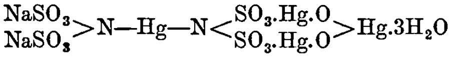
Normal *mercuric imidosulphonate* has not been isolated. According to E. Berglund, and E. Divers and T. Haga, when barium mercury imidosulphonate is treated with dil. sulphuric acid, in just sufficient quantity to remove the barium, it forms barium sulphate, and *mercury hydroimidosulphonate;* the latter begins to hydrolyze at once, and the soln. becomes turbid owing to the separation of **mercuric hydroimidodioxysulphonate,** $HN(SO_3)_2Hg_3O_2$, or



$$H{-}N{<}\begin{matrix}SO_3{-}Hg{-}O\\SO_3{-}Hg{-}O\end{matrix}{>}Hg$$

E. Berglund represented the formula $Hg\{N(HgSO_3)_2O\}_2$, but E. Divers and T. Haga think there is an error due to E. Berglund's product having been contaminated with potassium salt when prepared from dipotassium mercury imidosulphonate and mercuric nitrate; E. Divers and T. Haga's product was obtained from trisodium imidosulphonate and mercuric nitrate. Conc. soln. of mercuric nitrate, even when freed as much as possible from nitric acid, dissolve potassium or sodium imidosulphonates, forming clear, stable soln.; if these soln. are heated the imidosulphonate hydrolyzes into amidosulphonate, but if diluted without heating, they deposit the mercuric hydroimidodisulphonate. The same salt is precipitated on adding a cold soln. of one part trisodium imidosulphonate to a cold soln. of 5 parts of mercuric nitrate. Precipitation of the salt begins almost at once, and is finished in a few minutes. The mother-liquor still contains much mercuric nitrate and some imidodisulphonate, besides sodium nitrate and much nitric acid. The addition of a little more trisodium salt causes scarcely any further precipitation, but a larger quantity throws down the hydroimidodioxysulphonate. The brilliant white and voluminous hydroimidoxysulphonate hydrolyzes only very slowly in its acid mother-liquor, on account of the protective action of the mercuric nitrate. It should be repeatedly washed by subsidence and decantation with an abundance of cold water, and drained till dry on a tile or filter. If less mercuric nitrate has been used, and the precipitate contains sodium (as disodium mercuric imidodioxysulphonate), this may be converted into the pure hydroimidodioxysulphonate either by digestion for a day with conc. mercuric nitrate soln. and washing, or simply by continued and thorough washing with water. If digestion with mercury nitrate soln. is adopted, the water used for the first washing must contain a little nitric acid to guard against the formation of any oxynitrate. The reaction is symbolized $3Hg(NO_3)_2+Na_3N(SO_3)_2+2H_2O=HN(SO_3)_2Hg_3O_2+3NaNO_3+3HNO_3$, and it can be regarded as involving the formation of sodium mercury imido-oxysulphonate, $NaN(SO_3)_2Hg_2O$, which reacts with the mercuric nitrate: $Hg(NO_3)_2+NaN(SO_3)_2Hg_2O+H_2O=NH(SO_3)_2Hg_3O_2+NaNO_3+HNO_3$. This salt is anhydrous; it loses 0·7–0·8 per cent. of absorbed water at about 100°; and it may be heated to 180° without change, but at dull redness it decomposes, giving off water, nitrogen, and sulphur dioxide; at the softening temp. of hard glass, it melts to a red liquid and effervesces, yielding sublimates of mercury, mercurous and mercuric sulphates, etc. Even in vacuo, the salt does not decompose completely before the mercury sulphates themselves begin to decompose. The salt reacts with sodium hydroxide and chloride, and with trisodium imidosulphonate similar to sodium mercury imidoxysulphonate (*vide infra*). E. Berglund tried to make *ammonium mercuric imidodisulphonate* by the action of ammonium sulphate on barium mercury imidosulphonate, and E. Divers and T. Haga, by the action of ammonium hydrocarbonate on calcium mercury imidosulphonate. The precipitate consisted of calcium carbonate and *calcium mercuric imidotetraoxysulphonate*, $Ca(SO_3)_2N.Hg.N(SO_3HgO)_2Hg$. The ammonium mercuric salt thus appears incapable of continued existence. There are two sodium mercury imidosulphonates —one is the normal salt, the other is basic. E. Divers and T. Haga found that unless gradually added to the soln. of the trisodium salt, mercuric nitrate causes the immediate formation of a white, flocculent, crystalline precipitate which disappears on agitation so long as there is enough sodium salt present to keep the mixture neutral; when this point is just passed, the precipitate is permanent, and consists of sodium mercuric imidodioxysulphonate, $(NaSO_3)_2N.Hg.N(SO_3HgO)_2Hg$. If the nitrate is added until neutrality is just reached, or nearly reached, the soln. soon begins to deposit small, brilliant crystals, or does so after evaporation. These crystals are **disodium mercuric imidodisulphonate,** $Hg\{N(NaSO_3)_2\}_2.5H_2O$. The salt was first prepared by E. Berglund. The addition of a soln. of the trisodium salt to one of mercuric nitrate, free from any unnecessary excess of nitric acid, produces a flocculent precipitate of mercuric hydroimidosulphonate (*vide supra*). If there is too little nitrate, some sodium mercuric imidoxysulphonate will be deposited as well. Disodium mercuric imidosulphonate forms small prisms which are permanent in air, and sparingly soluble in cold water. Four mols of water are lost at ordinary temp. in vacuo, and most of the remaining water is lost at 100°. The residue slowly increases in weight at 130°, for it reacts with atm. moisture, and becomes hydrolyzed. When heated more strongly in an open tube, it yields a sublimate consisting mainly of ammonium sulphite, along with mercury, mercurous sulphate, sulphur dioxide, and nitrogen. The residue contains mercurous, mercuric, and sodium sulphates. In vacuo, no marked change occurs even at 440°, but just below red-heat, there is a steady decomposition: $2HgN_2(NaSO_3)_4=4Na_2SO_4+HgSO_4+HgS+2SO_2+2N_2$; and on further heating, $2HgN_2(NaSO_3)_4=4Na_2SO_4+2Hg+4SO_2+2N_2$. Soln. of ordinary metallic salts form a number of complex mercuric imidosulphonates studied by E. Berglund. Thus, barium chloride forms barium mercury imidosulphonate. Sodium hydroxide precipitates mercuric oxide incompletely from the pure salt soln., but not in the presence of sodium imidosulphonate. Ammonia, and ammonium chloride give white precipitates. Mercuric oxide dissolves slightly in an aq. soln. of disodium mercury imidosulphonate rendering the soln. alkaline. Both nitric and hydrochloric acids dissolve the salt freely, but the former acid does not decompose the salt immediately, while the latter does so completely, forming mercuric sodium chloride, sodium hydrosulphate, and amidosulphonic acid.

The formation of **disodium mercuric imidodioxysulphonate,**



$$\begin{matrix}NaSO_3\\NaSO_3\end{matrix}>N-Hg-N<\begin{matrix}SO_3.Hg.O\\SO_3.Hg.O\end{matrix}>Hg.3H_2O$$

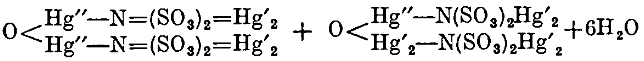
has been discussed above. Two molar proportions of the trisodium salt are used for one of mercuric nitrate. It was first made by E. Berglund. E. Divers and T. Haga represent the reaction $4Hg(NO_3)_2+2NaN(NaSO_3)_2+2H_2O=4NaNO_3+4HNO_3+Hg(OHgSO_3)_2NHgN(NaSO_3)_2$.

When the attempt was made to prepare an intermediate salt, *disodium mercuric imidoxysulphonate*, $\{HgN(SO_3Na)_2\}O$, the reaction appeared to be $6NaN(NaSO_3)_2+6Hg(NO_3)_2+4NaOH=2HgN_2(NaSO_3)_4+Hg(OHgSO_3)_2N.Hg.N(NaSO_3)_2+12NaNO_3+2H_2O$.

Disodium mercuric imidodioxysulphonate contains water of crystallization, and appears to be slightly efflorescent. Protracted washing with water decomposes it, leaving a residue of the hydroimido-dioxysulphonate: $2Hg(OHgSO_3)_2N.Hg.N(NaSO_3)_2+H_2O=2NH(SO_3HgO)_2Hg+\{HgN(NaSO_3)_2\}_2O$. A similar result is obtained by the action of a conc. soln. of mercuric nitrate. At 135°, the colour changes permanently, and at a higher temp. the salt forms a reddish-brown liquid and effervesces. The decomposition resembles closely that with the normal disodium mercury salt. Gradual heating in a current of dry air at 170° does not expel all the water, presumably owing to hydrolysis. The salt is more readily dissolved by hydrochloric acid than by nitric or sulphuric acid; the salt is decomposed at once by the hydrochloric acid as it is in the case of the normal disodium mercury salt. Sodium hydroxide forms insoluble mercuric oxide, and disodium mercuric imidosulphonate which remains dissolved. A soln. of trisodium imidosulphonate dissolves a little disodium mercuric imidodioxysulphonate. E. Berglund prepared what was probably **dipotassium mercuric imidodisulphonate,** $Hg\{N(KSO_3)_2\}_2$, and reported that it is not affected by nitric acid; but E. Divers and T. Haga found that it is thus converted into mercuric nitrate and dipotassium imidosulphonate.

E. Berglund failed to make **calcium mercuric imidosulphonate** on account of the solubility of the salt; but E. Divers and T. Haga obtained it in small prismatic crystals by dissolving mercuric oxide in a warm soln. of calcium imidosulphonate, and evaporating the filtered soln. for crystallization. When mercuric hydroimidodioxysulphonate is digested with a soln. of calcium chloride, small crystals of **calcium mercuric imidochlorosulphonate,** $(NS_2O_6Ca)_3HgCl_2.12H_2O$, were found. E. Berglund also prepared **strontium mercuric imidodisulphonate,** $N_2Hg\{(SO_3)_2Sr\}_2.5H_2O$, by treating a conc. soln. of the potassium mercuric salt with strontium nitrate. The clear crystals are microscopic needles or rhombic plates. They are more soluble in water than the potassium salt. When suspended in water, and treated with hydrogen sulphide there is formed a soln. of *strontium hydroimidosulphonate,* $\{Sr(SO_3)_2\}NH$, which decomposes when the attempt is made to isolate the salt. E. Divers and T. Haga made crystals of **barium mercuric imidodisulphonate,** $N_2Hg\{(SO_3)_2Ba\}_2$, from sodium mercuric imidosulphonate. The salt is but sparingly soluble in water. E. Berglund made the *pentahydrate* by the process used for the analogous strontium salt; and also by the action of barium nitrate on mercuric imidosulphonate. The crystals resemble those of the strontium salt. The salt is fairly stable when heated; it is almost insoluble in water. It is not attacked by dil. nitric acid, but is soluble in conc. nitric acid. Conc. hydrochloric acid dissolves it freely; and with sulphuric acid it forms mercuric imidosulphonate. E. Berglund made **magnesium mercuric imidodisulphonate,** $HgN_2\{Mg(SO_3)_2\}_2.15H_2O$, as in the case of the sodium salt using as little water as possible. The temp. during evaporation must not exceed 30°, and radiating masses of crystals are formed. The salt is unstable, and cannot be crystallized without decomposition; it decomposes below 100°, passing into a sulphate; and it is easily soluble in water.

E. Berglund found that when potassium mercuric imidosulphonate is added to a soln. of mercurous nitrate, some mercuric hydroimidoxysulphonate is deposited only after long standing. E. Divers and T. Haga said that some nitric acid must have been present, because precipitation is immediate when that acid is absent. The composition varies within the limits expressed by *mercurosic imidoxysulphonate,* $O\{Hg''N(SO_3)_2Hg'_2\}_2.3H_2O$, and the more complex mercurosic salt:

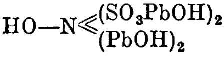


$$O{<}\begin{matrix}Hg''{-}N{=}(SO_3)_2{=}Hg'_2\\ Hg''{-}N{=}(SO_3)_2{=}Hg'_2\end{matrix} + O{<}\begin{matrix}Hg''{-}N(SO_3)_2Hg'_2\\ Hg'_2{-}N(SO_3)_2Hg'_2\end{matrix}+6H_2O$$

The former is produced by adding disodium mercuric imidosulphonate to half its weight of normal mercurous nitrate; and the latter by using these two components in the proportion 2 : 5.

V. A. Jacquelain, and E. Berglund used a lead imidosulphonate in order to prepare the acid. E. Divers and T. Haga could not prepare the normal salt *trilead* *imidosulphonate*, $Pb_3N_2(SO_3)_4$. The first addition of lead acetate or nitrate to a soln. of trisodium imidosulphonate gives a basic salt; and when the basic salt is treated with a little nitric acid, most of it passes into soln., while the undissolved part remains unchanged. If one of the basic salts of lead imidosulphonate be treated with less than sufficient dil. sulphuric acid to make **lead hydroimidodisulphonate,** $HN(SO_3)_2Pb$, the clear decanted soln. contains this salt in soln., but attempts to isolate it lead to its decomposition. This unstable soln. was also made by E. Berglund. According to E. Divers and T. Haga, in the absence of acetates, the soln. can be preserved for only a short time; in a desiccator, the soln. decomposes into amidosulphonic acid and lead sulphate—slowly at first, but rapidly as the liquid becomes conc. A similar change occurs when the soln. is heated. The soln. is slightly acid to litmus, and it produces with alcohol a voluminous precipitate, which gradually becomes crystalline, and which appears to be lead sulphate.

According to E. Divers and T. Haga, if lead nitrate and trisodium imidosulphonate in soln. are mixed in widely varying proportions, **lead trihydroxyimidodisulphonate,** $HOPb.N(SO_3PbOH)_2$, is precipitated: $3Pb(NO_3)_2+3H_2O+4Na_3N(SO_3)_2=(HOPb)_3N(SO_3)_2+3HN(SO_3Na)_2+6NaNO_3$. The voluminous precipitate soon becomes dense and granular. The results are not so satisfactory with lead acetate in place of the nitrate. The disodium salt which is formed reacts with the excess of lead acetate: $3Pb(C_2H_3O_2)_2+3H_2O+HN(NaSO_3)_2=(PbOH)_3N(SO_3)_2+2NaC_2H_3O_2+4C_2H_4O_2$. The acetic acid so generated acts in reversing the reaction. This salt was also prepared by E. Berglund, and E. Divers and T. Haga said that it can be prepared in a high degree of purity by treating lead pentahydroxyimidosulphonate with but a little more nitric acid than is needed to remove the excess of lead. The reaction is said to occur in two stages: $(PbOH)_3N(SO_3)_2Pb(OH)_2+6HNO_3=HNPb(SO_3)_2+5H_2O+3Pb(NO_3)_2$; and the soln. then reacts with more of the basic salt: $2(PbOH)_3N(SO_3)_2Pb(OH)_2+HNPb(SO_3)_2=H_2O+3(PbOH)_3N(SO_3)_2$. The trihydroxyimidosulphonate has also been made by the action of disodium imidosulphonate on lead pentahydroxyimidosulphonate. The trihydroxyimidosulphonate forms microscopic, prismatic crystals which are anhydrous; they lose nothing at 100°; are insoluble in water; and give but a slight alkaline reaction in contact with moist litmus paper. E. Divers and T. Haga reported **lead pentahydroxyimidodisulphonate,** $Pb_4(OH)_5N(SO_3)_2$, or



$$HO—N\lessdot\begin{matrix}(SO_3PbOH)_2\\(PbOH)_2\end{matrix}$$

to be formed by adding trisodium imidosulphonate to a large excess of basic lead acetate: $Na_3N(SO_3)_2+5(HO)Pb(C_2H_3O_2)=3NaC_2H_3O_2+Pb(C_2H_3O_2)_2+(PbOH)_3N(SO_3)_2Pb(OH)_2$. This salt was made by E. Berglund by gradually adding aq. ammonia to a mixed soln. of the diammonium salt and lead acetate so long as the amorphous precipitate first produced gives place to a crystalline one. When the amorphous precipitate no longer changes, acetic acid is added until nothing but a crystalline precipitate is present. E. Berglund said that the precipitate has a variable composition; E. Divers and T. Haga found their product has a uniform composition. The precipitate is insoluble in water, readily soluble in dil. nitric acid (*vide supra*), has scarcely any action on moist red litmus; it is insoluble in soln. of the parent salts; it does not lose water at 130°, but at higher temp. it decomposes: $3(OH)_5Pb_4N(SO_3)_2=6PbO+3PbSO_3+3PbSO_4+NH_3+N_2+6H_2O$. The mass then blackens through the conversion of the lead sulphite to sulphate and to lead oxide and sulphur dioxide.

F. Ephraim and W. Flügel prepared sparingly soluble **cobalt hexammino-imidodisulphonate,** $[Co(NH_3)_6]_2.\{NH(SO_3)_2\}_3$; **cobalt aquopentamminoimidodisulphonate,** $[Co(NH_3)_5(H_2O)]_2\{NH(SO_3)_2\}_3$; and **cobalt nitritopentamminoimidodisulphonate,** $[Co(NH_3)_5(H_2O)]NH(SO_3)_2$.

H. Kirmreuther prepared **tetrapotassium trans-dichlorodiimidodisulphonatoplatinite,** $[Cl_2Pt(NH.SO_3)_2]K_4$, by dissolving potassium trans-dichloroimidosulphonatoplatinite in potassium hydroxide, and precipitating the soln. with alcohol. The yellow radiating clusters of prisms form a strongly alkaline soln. with water.

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§ 54. Thionyl and Sulphuryl Amides, Imides, and Hydrazides

H. Schiff[1] thought that he had made **thionyl amide**, $SO(NH_2)_2$, by the action of thionyl chloride on ammonia, but A. Michaelis showed that the yellow product so obtained was only a mixture of nitrogen sulphide, and ammonium tri- and tetra-thionates. A. Mente obtained a similar product by the action of ammonium carbonate on thionyl chloride.

According to W. Traube,[2] when sulphuryl chloride in chloroform soln. is treated with ammonia, there is formed (i) sulphuryl amide, $SO_2Cl_2+4NH_3=2NH_4Cl+SO_2(NH_2)_2$; (ii) sulphuryl imide, $SO_2Cl_2+3NH_3=2NH_4Cl+SO_2(NH)$; and (iii) probably imidosulphuryl amide, $2SO_2Cl_2+7NH_3=4NH_4Cl+NH(SO_2.NH_2)_2$, because ammonium imidosulphonate was present in an aq. soln. of the products of the reaction. A. Hantzsch and co-workers also obtained several by-products when ligroin was used in place of chloroform as solvent. H. V. Regnault prepared **sulphuryl amide**, or *sulphamide*, $SO_2(NH_2)_2$, admixed with ammonium chloride, by the action of dry ammonia on a mixture of sulphuryl chloride and ethylene chloride in the cold. W. Traube recommended the following mode of preparation:

Well-cooled sulphuryl chloride, diluted with 15–20 vols. of chloroform, is sat. with dry ammonia, the precipitated product dissolved in water, the soln. acidified with nitric acid, and the whole of the chlorine precipitated with silver nitrate; the filtered soln. is neutralized with alkali, treated with silver nitrate, and the crystalline precipitate, which consists of silver sulphimide and some other silver derivative, separated by filtration. After adding a further quantity of silver nitrate, the clear soln. is treated with alkali, when silver sulphamide is obtained as a colourless, amorphous precipitate, which, however, is invariably mixed with some other silver compound, probably the same as that present in the silver sulphimide precipitate. In order to remove this impurity, the well-washed precipitate is treated with hydrochloric acid in quantity exactly sufficient to convert the silver into chloride, and the strongly acid soln. is neutralized with ammonia and mixed with silver nitrate, when only the silver compound of unknown composition is precipitated; pure silver sulphamide can now be precipitated by adding silver nitrate and excess of ammonia, and on decomposing this compound with the necessary quantity of hydrochloric acid, a neutral or feebly acid soln. of sulphamide is obtained. Sulphamide is deposited in large, colourless crystals when its aq. soln. is evaporated over sulphuric acid under reduced press.

A. Hantzsch and A. Holl recommended purifying the compound by crystallization from hot ethyl alcohol. A. Mente found it among the products of the action of ammonium carbonate on sulphuryl chloride; and F. Ephraim failed to obtain it during the action of urethane on sulphuryl chloride. E. Divers and M. Ogawa observed the formation of this compound in the spontaneous decomposition of ammonium sulphinate.

The ammonium sulphinate is prepared as indicated in connection with that salt, and, without removing the product from the flask in which it was made, a slow current of hydrogen was passed through the flask while immersed in a water-bath and gradually warmed to 70°. This temp. is maintained for 6–7 hrs. so as to drive off all the ammonia. The sulphuryl amide is formed at 30°–35°, and the higher temp. is used to destroy the thionic compounds as much as possible. If the temp. exceeds 70°, the sulphuryl amide is decomposed. The products of the reaction are then dissolved in enough ice-cold water to dissolve everything except the sulphur; and conc. barium hydroxide is added to the unfiltered soln. This precipitates the sulphates, imidosulphinates, and thiosulphates. The filtrate, which is more or less turbid, is treated with silver nitrate until precipitation no longer obtains. The filtrate is neutralized with ammonia, and the small precipitate removed. The filtrate contains sulphuryl amide and ammonium amidosulphonate. The former is precipitated by the addition of ammonia and silver nitrate, and the silver sulphamide treated as in W. Traube's process—*vide supra.*

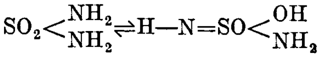
F. Ephraim and M. Gurewitsch said that sulphamide of a high degree of purity is made by dissolving the product of the reaction between sulphuryl chloride and liquid ammonia in a small quantity of water and making the soln. just acid. After two or three days the hydrolysis is complete, the mixture is evaporated to dryness in a vacuum, and the residue extracted with ethyl acetate, which dissolves out the sulphamide, amidosulphonic acid and ammonium chloride being insoluble. After evaporating off the ethyl acetate, pure sulphamide, m.p. 93°, is left.

The colourless, rhombic, tabular crystals are quite tasteless and leave a cooling sensation on the tongue. W. Traube said that they sinter at 75°, and melt at 81°, while A. Hantzsch and A. Holl gave 91·5°, and F. Ephraim and M. Gurewitsch, 93°, for the m.p. W. Traube said that when heated above the m.p., sulphuryl amide begins to give off ammonia, and it decomposes completely with the evolution of acid vapours when heated above 250°. A. Hantzsch and B. C. Stuer found that when heated above its m.p., it forms sulphuryl imidodiamide, and not trisulphuryl imide. A. Hantzsch and A. Holl said that sulphuryl amide is not an electrolyte, and its aq. soln. conducts very badly. The lowering of the f.p. of water by sulphuryl amide agrees with the mol. wt. 96·8—theory for $SO_2(NH_2)_2$ requires 96·2. The compound is therefore unimolecular and built on the carbamide type. W. Sarow found the mol. electrical conductivity, μ, of a mol of sulphuryl amide in v litres of water at 25° to be:

v . . .	32	64	128	256	512	1024
μ . . .	17·0	18·8	20·1	21·1	22·9	30·2

He also measured the conductivity in soln. of hydrochloric acid, sodium hydroxide, and aq. ammonia, and inferred that the sulphuryl amide has the character of an acid—*vide supra,* amidosulphinic acid. Sulphuryl amide has a neutral reaction. It is readily soluble in water. Boiling acids decompose it, forming sulphuric acid and ammonia; but when treated with alkali-lye, amidosulphonic acid. It is decomposed by nitrous acid in the cold, forming sulphuric acid. E. C. Franklin and O. F. Stafford said that sulphuryl amide rapidly absorbs gaseous ammonia, and readily dissolves in liquid ammonia. The soln. so formed yields two potassium salts when treated with potassium. According to F. Ephraim and E. Lasocky, sulphamide readily dissolves in cold, conc. nitric acid, of sp. gr. 1·48, without being decomposed or nitrated. Nitration takes place immediately, however, if conc. sulphuric acid is added to the soln., the nitrito-compound thus formed precipitating in the solid form. It is necessary to avoid any rise in temp. during the reaction and to work with a small quantity only, since the **nitritosulphamide,** $NH_2.SO_2.NH(NO_2)$, formed very readily decomposes with explosive violence when present in large quantity. When dry, it is much more stable than when moist. As so prepared, it is fairly pure, and it may be further purified from ether. When heated carefully, it decomposes quietly at 95°–96°, but ordinarily it decomposes with a slight puff, without detonation, white vapours being evolved. The formula is confirmed by the analysis of the **silver nitritosulphamide,** $NHAg.SO_2.NAg.NO_2$, which is obtained as a flocculent, white precipitate when silver nitrate is added to the aq. soln. of the nitritosulphamide, and then ammonia until the precipitate no longer increases in vol. Hydrogen is evolved when zinc dust is added to the aq. soln. of nitrosulphamide, the zinc salt being formed. If the soln. is then acidified with sulphuric acid, complete reduction to **hydrazinesulphamide,** $NH_2.SO_2.NH.NH_2$, occurs. The reaction does not stop at this point, but proceeds further, forming amidosulphonic acid, and hydrazinosulphonic acid—*vide infra*—or their zinc salts. The zinc salt of the latter is much more soluble than the zinc salts of the former. If the nitric acid soln. of sulphamide is well cooled, the addition of a few drops of sulphuric acid may give a white, deliquescent precipitate, which is probably a **nitratosulphamide.** W. Traube found that the compound is insoluble in ethyl alcohol, ether, and some other organic liquids; but it is perceptibly soluble in cold and readily soluble in hot methyl or ethyl alcohol.

W. Traube and E. Reubke found that sulphuryl amide dissolves 1·4 mol. proportions of ammonia at 20°; 3·0, at 0°; and 5·4 at −20°. The product has an electrical conductivity 150 times that of a 4*N*-aq. soln. of sulphuryl amide; and the conductivity is 25 times that of a 4*N*-soln. of ammonia alone. It is therefore assumed that sulphuryl amide can exist in an *aci*-form:



$$SO_2{<}{}^{NH_2}_{NH_2} \rightleftharpoons H{-}N{=}SO{<}{}^{OH}_{NH_2}$$

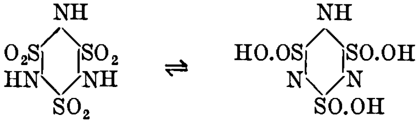
Sulphuryl amide. Sulphamidic acid.

as in the case of carbamide. **Sodium sulphamidate,** $HN : SO(NH_2)ONa$; **lithium, potassium, barium, and calcium sulphamidates** were prepared in colourless, non-hygroscopic crystals. Similarly, **copper tetramminosulphamidate,** $\{HN : SO(NH_2)O\}_2Cu.4NH_3$; and **copper ethylenediaminosulphamidate** were obtained as blue crystals. They also prepared *benzylidene sulphamide,* $NH_2.SO_2.N : CH.C_6H_5$.

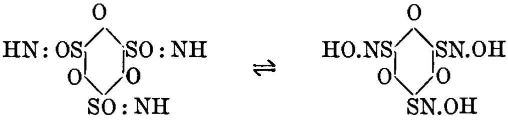
F. Ephraim and M. Gurewitsch made **amidosulphuryl chloride,** or **sulphuryl chloroamide,** $Cl\,SO_2.NH_2$, by the action of thionyl chloride on amidosulphonic acid—*vide supra;* they also found that amidosulphonic acid and phosphorus pentachloride, in the proportion of 1 : 5 by weight, readily interacted at 70-90°. After filtering the olive-green liquid so obtained through glass wool, it was distilled on the water-bath under diminished press. Phosphoryl chloride and phosphorus trichloride passed over, leaving a viscous, dark brown liquid, which deposited white crystals (m.p. 33°–34°)—after a long time at 0°. W. Traube and E. Reubke obtained it by the action of hypochlorous acid on sulphuryl amide, and gave its m.p. as 66° without decomposition. The analytical results were only in approximate agreement with the formula $NH_2.SO_2.Cl.PCl_3$, **amidosulphuryl phosphorous tetrachloride.** The compound is very sensitive to water vapour, hydrogen chloride, phosphorous acid, and amidosulphonic acid being formed. Boiling sodium hydroxide does not liberate ammonia, which is only produced on prolonged heating with fuming hydrochloric acid in a sealed tube. All attempts to decompose it into its components were unsuccessful.

W. Traube prepared **silver sulphamide,** $SO_2(NHAg)_2$, by digesting sulphuryl amide with ammonia and silver nitrate. The compound was also prepared by E. Divers and M. Ogawa, and A. Hantzsch and A. Holl. F. Ephraim and M. Gurewitsch found that dimethyl sulphate and ammonia, instead of giving sulphuryl amide, formed methylamine and ammonium methyl sulphate. They found that silver sulphimidodiamide is readily transformed with silver sulphamide by soln. in dil. acid, and precipitation from the warm soln. by ammonia: $NH(SO_2.NH_2)_2+H_2O=NH_2(HSO_3)+SO_2(NH_2)_2$. If ammonium chlorosulphonate be treated with liquid ammonia; and the residue after the evaporation of the ammonia be acidified with nitric acid; treated with silver nitrate; and the filtrate fractionally precipitated with ammonia, hot soln. yield silver sulphamide, and cold soln. silver sulphimidoamide. It is a colourless, amorphous powder, only slightly sensitive to light; it has an alkaline reaction, and dissolves freely in nitric acid and ammonium carbonate, but is sparingly soluble in cold water. It loses ammonia when heated, and decomposes completely at about 200° with evolution of sulphurous anhydride; it reacts with alkyl iodides and with acid chlorides, and its aq. soln. gives precipitates with mercuric nitrate—**mercury sulphamide**—and lead acetate—**lead sulphamide.** A. Hantzsch and A. Holl found that it is insoluble in pyridine, and forms unsymmetrical *dimethyl sulphamide* when treated with methyl iodide; W. Sarow also prepared a number of sulphamides.

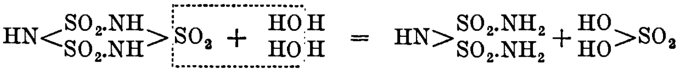
W. Traube described the formation of what he called *sulphimide*, along with ammonia and imidosulphonic acid, when sulphamide is heated at 200°–210°. The solid product is treated with water, the soln. mixed with silver nitrate, and the precipitated silver sulphimide, purified by recrystallization, is decomposed with dil. hydrochloric acid. The aq. soln. decomposes when the attempt is made to isolate the solid, for when the soln. is evaporated below 40°, only ammonium hydrosulphate remains. A. Hantzsch and A. Holl found the soln. in ethyl acetate has properties in accord with the trimolecular formula **sulphuryl triimide**, or *trisulphimide*, $(SO_2.NH)_3$—*e.g.* ebulliscopic determinations of the mol. wt.; and the electrical conductivities of the aq. soln. of trisulphimide and its salts. They were able to isolate a crystalline solid by crystallization from ethyl alcohol which they considered to be trisulphimide itself. A. Hantzsch and B. C. Stuer, however, showed that the alleged compound is extremely unstable, and that the soln. obtained by W. Traube, and the solid obtained by A. Hantzsch and A. Holl, was really sulphuryl imidodiamide, only indications of the transient formation of trisulphimide in non-aqueous solvents were obtained. Trisulphimide acts as an acid, and a few salts have been reported. A. Hantzsch and B. C. Stuer consider that the compound has tautomeric forms—a true imide and an acid:



analogous with cyanuric acid. Trisulphimide may possibly be constituted on the cyamelide type, with the tautomeric forms:



The resolution of sulphimide into the imidoamide and sulphuric acid is symbolized



$$HN{<}\begin{matrix}SO_2.NH\\SO_2.NH\end{matrix}{>}\boxed{SO_2+\begin{matrix}HO\,H\\HO\,H\end{matrix}}=HN{>}\begin{matrix}SO_2.NH_2\\SO_2.NH_2\end{matrix}+\begin{matrix}HO\\HO\end{matrix}{>}SO_2$$

A. Hantzsch and B. C. Stuer reported **ammonium trisulphimide,** $(SO_2.N.NH_4)_3$, to be formed by passing ammonia into a soln. of the acid in acetic ether. The salt reported by W. Traube by the action of ammonia on sulphimide must have been the sulphimidodiamide. Similar remarks apply to the product obtained by A. Hantzsch and A. Holl. According to A. Hantzsch and B. C. Stuer, the gelatinous substance obtained by these workers as a by-product in the preparation of sulphamide by the action of ammonia on a soln. of sulphuryl chloride in ligröin was a mixture of ammonium chloride and **ammonium sulphimide,** $(SON)_3(OHN_4)_3$, of the melide-type. The mixture is difficult to separate. The product is soluble in dil. acids from which it is precipitated by alkali; the acid soln. is gradually decomposed by water. The salt is completely decomposed by heating it with conc. hydrochloric acid in a sealed tube at 150°. According to W. Traube, when the silver derivative—*vide supra*—is treated with an eq. quantity of a hot soln. of potassium chloride, well-defined colourless crystals of **potassium sulphimide,** $SO_2 : NK$, or $(SO_2 : NK)_3$, are formed. The salt is soluble in water; the soln. has a neutral reaction and is quite stable, but it is slowly decomposed by boiling acids. The dry salt decomposes when heated, glowing vividly, and leaving a residue of potassium sulphate and sulphite with the evolution of nitrogen and sulphur dioxide. A crystalline powder of **sodium sulphimide,** say $(SO_2 : NNa)_3$, was similarly obtained. It is soluble in water, and its properties resemble those of the potassium salt. A green amorphous powder of **copper sulphimide,** say $\{(SO_2 : N)_3\}_2Cu_3$, was also prepared. W. Traube made **silver sulphimide,** SO_2NAg, as represented by A. Hantzsch and A. Holl, $(SO_2NAg)_3$, by treating a soln. of silver sulphamide with silver nitrate, and heating the precipitated salt at 170°–180° until ammonia is no longer given off. The powdered material is ground up with an indifferent substance by barium sulphate or ammonium chloride, and heated to at first between 140° and 150°, and later between 170° and 180°. The mass is extracted with hot dil. nitric acid, and on cooling, silver sulphimide is obtained in acicular crystals, which can be purified by re-crystallization from water. It is sparingly soluble in cold water, more soluble in hot water, and very soluble in water acidulated with nitric acid. It decomposes completely when heated, forming silver and silver sulphate. A. Hantzsch and A. Holl prepared complexes with pyridine, $(SO_2NAg)_3.6C_6H_5N$. W. Traube made **calcium sulphimide,** $\{(SO_2N)_3\}_2Ca_3$, soluble in water; and **barium sulphimide,** $\{(SO_2N_3\}_2Ba_3.2H_2O$, in lustrous needles, which lose water when heated. The salt is freely soluble in water, and decomposed by boiling hydrochloric acid, forming barium sulphate. Silver nitrate produces a sparingly soluble precipitate with the aq. soln. A. Hantzsch and B. C. Stuer obtained the melide-type of barium sulphimide, $\{(SO_2N)_3\}_2Ba.5H_2O$, by the action of barium chloride on the ammonium salt. W. Traube also prepared **lead sulphimide,** presumably $\{(SO_2N)_3\}_2Pb$, which crystallizes from hot dil. alcohol in long needles. A. Hantzsch and A. Holl also made *methyl sulphimide,* $(SO_2NCH_3)_3$; and *benzoyl sulphimide,* $(SO_2N.CO.C_6H_5)_3$.

A. Mente reported **sulphuryl imidodiamide,** or *sulphimidodiamide,* or *imidosulphamide,* $NH_2.SO_2.NH.SO_2.NH_2$, or $HN(SO_2.NH_2)_2$, to be formed when ammonia acts on pyrosulphuryl chloride. This has not been confirmed. The substance which A. Hantzsch and A. Holl described as trisulphimide was shown by A. Hantzsch and B. C. Stuer to be sulphuryl imidodiamide. M. Gurewitsch obtained this compound by the action of sulphuryl chloride on liquid ammonia: $2SO_2Cl_2+7NH_3=NH(SO_2.NH_2)_2+4NH_4Cl$; and likewise by the action of amidosulphuryl chloride on the same menstruum: $2(NH_2.SO_2.Cl)+3NH_3=2NH_4Cl+NH(SO_2.NH_2)_2$. In preparing sulphuryl imidoamide, A. Hantzsch and A. Holl decomposed silver trisulphimide with hydrogen sulphide and crystallized the product from methyl alcohol; and A. Hantzsch and B. C. Stuer preferred to decompose the silver compound with anhydrous hydrogen cyanide, and to use ethyl acetate as the crystallizing agent:

Fifteen to twenty c.c. of thoroughly dried hydrogen cyanide at −12° were treated with 3 to 5 grms. of dried and powdered silver trisulphimide in small quantities at a time, with frequent agitation. The filtrate was rapidly washed with hydrogen cyanide, and the solvent evaporated in vacuo. The crystalline residue, protected from the moisture of the atm., was treated with dried ethyl acetate at 50°, and the filtrate evaporated in vacuo. The residue was pressed on porous tiles to remove oleaginous matters, washed with a little ethyl acetate, and crystallized from its soln. in dried ethyl acetate. The operation should be conducted in desiccators. The yield is only 5 per cent. of the silver trisulphimide employed.

The needle-like crystals have no colour or smell, but have a strong acidic taste. They are not readily dissolved by water, they are not hygroscopic, and are fairly stable. The compound is at once decomposed by water at 0° into amidosulphonic acid and sulphuryl amide: $HN(SO_2.NH_2)_2+H_2O=SO_2(NH_2)_2+NH_2.HSO_3$. The mol. wt. determinations of the salt in aq. soln., and the electrical conductivity confirm this reaction. The electrical conductivity of aq. soln. gives values corresponding with those for amidosulphonic acid, since the sulphuryl amide also produced is not an electrolyte. The compound is insoluble in benzene, and chloroform;

sparingly soluble in ether, cold and hot ethyl acetate, and acetic acid. It is soluble in cold ethyl or methyl alcohol, and more so when heated.

Sulphuryl imidodiamide is moderately stable towards alkalies, and it acts as a monobasic acid, forming salts of the type $(NH_2.SO_2)_2NM$. It is not certain whether the metal is directly attached to the nitrogen. A. Hantzsch and B. C. Stuer found that when sulphuryl imidodiamide is mixed with finely divided glass, and exposed to dry ammonia, about 20 per cent. of gas is absorbed; if the product be kept in a desiccator until its weight is constant, **ammonium sulphimidodiamide,** $(NH_2.SO_2)_2N(NH_4)$, is formed. The same salt is produced when a soln. of sulphuryl imidodiamide in liquid ammonia is evaporated in vacuo. Its m.p. is 117°. When sulphuryl imidodiamide is gradually added towards an excess of an aq. soln. of potassium hydroxide, the **potassium sulphimidodiamide,** $(NH_2.SO_2)NK$, first formed gradually decomposes—one-third of the total nitrogen being evolved as ammonia, and an amidosulphonate is formed: $H_2O+KOH+(SO_2.NH_2)_2NK \rightarrow NH_3+2K(NH_2SO_3)$. Hence, alkali-lye does not hydrolyze sulphuryl imidodiamide to ammonium imidosulphonate as supposed by A. Mente. There are similar indications of the formation of *barium sulphimidodiamide*, by the action of baryta-water. It was also found that **silver imidodiamide,** $(NH_2.SO_2)_2NAg.1\frac{1}{2}H_2O$, obtained by adding sulphuryl imidodiamide, to an excess of silver carbonate or of silver oxide suspended in water, is not acted on by cold conc. aq. potassium hydroxide with the formation of ammonia; it separates from a mixture of ether and pyridine in stellate crystals. When acted on by acids, it forms mol. proportions of amidosulphonic acid and sulphonamide. It is formed in small amount during the preparation of silver trisulphimide. It is sometimes formed in rhombohedra. F. Ephraim and M. Gurewitsch found that silver sulphimidodiamide is obtained from ammonium chlorosulphonate as indicated above. When sulphuryl chloride is added drop by drop to liquid ammonia cooled by an ether-solid carbon dioxide freezing mixture, there is a violent reaction according to the equation: $2SO_2Cl_2+7NH_3 = NH(SO_2.NH_2)_2+4NH_4Cl$. No trisulphimide is formed, and, after evaporating off the excess of ammonia, silver imidosulphamide may be obtained from the residue in a manner similar to that already described. It is always contaminated with silver sulphamide, the sulphamide being formed from the sulphuryl imidodiamide according to the equation: $NH(SO_2.NH_2)_2+H_2O = NH_2.SO_3H+SO_2(NH_2)_2$. In fact, silver sulphimidodiamide may be readily transformed into silver sulphamide by soln. in dil. acid and precipitation from the warm soln. by ammonia. Pure silver sulphimidodiamide was prepared by extracting the product of the reaction between sulphuryl chloride and liquid ammonia with ethyl acetate in order to remove the sulphamide, and then working up the residue at the ordinary temp. to silver sulphimidodiamide in the manner already indicated.

Instead of working with an excess of sulphuryl chloride, F. Ephraim and F. Michel worked with an excess of ammonia, adding a soln. of sulphuryl chloride in ligröin to a soln. of ammonia in the same solvent, while a current of ammonia gas is passing so as to keep the ammonia in excess. The products of the reaction are different in this case; very little sulphuryl amide, or trisulphimide is formed. The chief products are sulphuryl imidoamide, and long chain products involving four SO_2-groups—*e.g.* $NH_2.SO_2.NH.SO_2.NH.SO_2.NH.SO_2.NH_2$—and these form sulphuryl imide only by secondary reactions. The different substances were isolated as silver salts. The product of reaction in the light petroleum was dissolved in water, and the soln. digested with freshly precipitated lead hydroxide to remove the ammonium chloride. After cooling and filtering, the filtrate was acidified with nitric acid, and the remaining chlorine precipitated with silver nitrate. After collecting the silver chloride, the filtrate was fractionally precipitated by ammonia. The first fraction was obtained by adding ammonia until the white, flocculent precipitate began to ball together, and then stirring for some minutes. The filtrate from this reacted acid; excess of ammonia was added, and the second and chief reaction was obtained. The filtrate was again acid, and gave a further precipitate of unimpure product (not further investigated) on neutralizing with ammonia. The silver salts were all amorphous, and contained irregularly varying amounts of water; they were very difficult to purify.

The first fraction furnished a white powder only slightly affected by light; and it corresponded with $Ag_2N.SO_2.NAgSO_2.NHSO_2.NAg.SO_2.NAg_2$, *i.e. hexasilver tetrasulphuryltrimidodiamide*, or $Ag_2N.SO_2.NH.SO_2.N(SO_2.NAg)_2$. The first fraction contained what was considered to be an equimolar mixture of silver sulphamide, and silver sulphimidamide. It gives an addition product with pyridine. By fractionation still more, the salts $(SO_2)_4N_5Ag_8H.2H_2O$, or $Ag_2N.SO_2.NAg.SO_2.NH.SO_2.NAg.SO_2.NAg_2$, *hexasilver tetrasulphuryltriimidodiamide*; $(SO_2)_4N_5Ag_78H_2O$, or $Ag_2N.SO_2.NAg.SO_2.NAgSO_2.NAg.SO_2.NAg_2$, *heptasilver tetrasulphuryltriimidodiamide*, $(SO_2)_3N_5H_6Ag_3.5\frac{1}{2}H_2O$, or $AgNH.SO_2.NAg.SO_2.NAg.SO_2.NH(NH_4)$, *ammonium trisilver trisulphuryldiimidodiamide*; and $(SO_2)_4N_7Ag_5H_8.4H_2O$, which may be a mixture of silver sulphamide and sulphimidamide, or $(NH_4)NAg.SO_2.NAg.SO_2.NAg.SO_2.NAg.SO_2.NAg(NH_4)$, *i.e. diammonium pentasilver tetrasulphuryltrimidodiamide.*

F. Ephraim and E. Lasocky found that sulphuryl chloride reacts with hydrazinecarboxylic acid, or preferably with hydrazine hydrazinecarboxylate, according to the equation: $SO_2Cl_2+2NH_2.NH.CO_2H,N_2H_4=SO_2(NH.NH_2)_2+2N_2H_4,HCl+2CO_2$, forming **sulphuryl hydrazide**, $SO_2(NH.NH_2)_2$. The hydrazine hydrazinecarboxylate is suspended in light petroleum or carbon tetrachloride, and the sulphuryl chloride gradually added, the mass obtained being well kneaded in order for the reaction to become complete. It was not found possible to obtain the pure sulpho-hydrazide, owing to the difficulty of separation from the accompanying hydrazine hydrochloride, but the **hydrazine sulphurylhydrazide**, $SO_2\{N(N_2H_5.NH_2)\}_2$, was obtained from the reaction product as follows: The reaction product was dissolved in water, and the soln. digested at 50° with freshly precipitated and washed lead hydroxide for several hours. The suspension of lead hydroxide is alkaline enough to prevent the decomposition of the sulphohydrazide, which is very sensitive towards acids. On evaporating the filtrate in vacuo an uncrystallizable syrup was obtained. The compound is stable in neutral or alkaline soln., but it readily decomposes in the presence of acids. It gives no precipitate with the salts of the heavy metals, except mercury. When the soln. is evaporated with lead nitrate ($\frac{1}{2}$ mol) a syrupy residue is left, from which hydrazine nitrate may be crystallized out by inoculation, leaving an oil corresponding with the formula of **lead hydrazine sulphurylhydrazide**, $Pb\{N(NH_2).SO_2.N(N_2H_5).NH_2\}_2$. A crystalline benzoyl derivative, **sodium dibenzoyl sulphurylhydrazide**, $SO_2(NNa.NHBz)_2$, was obtained by the action of benzoyl chloride on the alkaline soln. of hydrazine sulphohydrazide.

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§ 55. Nitrosulphinic and Nitrilosulphonic Acids and their Salts

A. Claus[1] assumed that a series of substitution products are obtained in which the nitrogen is quinquevalent, thus, $N(HSO_3)_5$, *pentasulphammonic acid*; $NH(HSO_3)_4$, *tetrasulphammonic acid;* $NH_2(HSO_3)_3$, *trisulphammonic acid*; $NH_3(HSO_3)_2$, *disulphammonic acid;* and $NH_4(HSO_3)$, *monosulphammonic acid.* There is, however, very little support for the hypothesis, the first member is not known; the representative of the second member is based on what is now considered to have been a mixed product; the representative of the third member is dubious; the term disulphammic acid was applied to imidosulphonic acid which is now considered to have the constitution $H.N:(HSO_3)_2$; and the last member is represented by ammonium hydrosulphite, $(NH_4)(HSO_3)$. The replacement of the third hydrogen atom of ammonia by the sulphinic and sulphonic acid radicles furnishes the corresponding nitrilo-acids, in which the nitrogen nucleus is assumed to be tervalent. The first member, **nitrilosulphinic acid,** $N(HSO_2)_3$, has not been prepared. There is a possibility that H. Schumann produced **ammonium nitrilosulphinate,** $N(SO_2NH_4)_3$, with the ultimate composition $4NH_3.3SO_2$, by boiling a soln. of amidosulphinic with carbon disulphide in a reflux condenser with the careful exclusion of moisture; ammonia is given off, and a dark red crystalline sublimate of this compound is formed. It is very hygroscopic, and is decomposed by water with the evolution of ammonia. E. Divers considers the alleged compound to be a mixture of the decomposition products of ammonium amidosulphinate (*q.v.*).

E. Divers and T. Haga [2] have shown that there is an interesting list of compounds of ammonia with sulphur trioxide, namely:

[$NH_3.3SO_3$, *i.e.* $N(HSO_3)_3$	Nitrilotrisulphonic acid]
$NH_3.2SO_3$, *i.e.* $NH(HSO_3)_2$	Imidosulphonic acid
$NH_3.SO_3$, *i.e.* $NH_2(HSO_3)$	Amidosulphonic acid
$4NH_3.3SO_3$, *i.e.* $N(NH_4SO_3)_3$	Ammonium nitrilosulphonate
$3NH_3.2SO_3$, *i.e.* $HN(NH_4SO_3)_2$	Diammonium imidosulphonate
$4NH_3.2SO_3$, *i.e.* $(NH_4)N(NH_4SO_3)_2$	Triammonium imidosulphonate
$2NH_3.SO_3$, *i.e.* $H_2N.SO_3NH_4$	Ammonium amidosulphonate

The first member of the series, **nitrilotrisulphonic acid,** $N(HSO_3)_3$, has not been isolated in the free state, although its ammonium salt is fourth on the list. The remainder can be derived from one another backwards or forwards. The **nitrilosulphonates** were discovered by E. Frémy in 1845 and called by him *sulphammonates*; in 1869, their sulphonic nature was established by A. Claus and S. Koch; and in 1875, E. Berglund demonstrated their nitrilic constitution and called them nitrilosulphonates. This was confirmed by F. Raschig in 1888. E. Divers and T. Haga called them *nitrilosulphates,* and suggested as possible names, *aminotrisulphonates,* and *trisulphamates.* E. Frémy called the acid *sulphammonic acid;* A. Claus, *trisulphammonic acid;* and A. Claus and S. Koch, *tetrasulphammonic acid.*

The nitrilosulphonates cannot be obtained by the union of ammonia and sulphur trioxide since the imidosulphonate is formed which is not resolved by heat into ammonia and nitrilosulphate. These salts are made by the sulphonation of the hydroxylamidosulphonates which E. Frémy accomplished by adding a nitrite to an excess of, say, potassium pyrosulphite when the potassium nitrilosulphonate crystallizes out, or by treating a hydroxylamidosulphonate with sulphur dioxide in presence of a base, a process which, in practice, resolves itself into treating the corresponding nitrite in this way since the hydroxylamidosulphonate is formed by the sulphonation of a nitrite. E. Frémy prepared **ammonium nitrilotrisulphonate,** $N(NH_4SO_3)_3.2H_2O$, by passing sulphur dioxide into a conc. soln. of ammonium nitrite mixed with a large excess of ammonia until an abundant precipitation of crystals occurs in the soln. kept sufficiently cool. The crystals were washed and dried. E. Frémy represented the salt as a monohydrate, but E. Divers and T. Haga showed that it is really a dihydrate; E. Frémy's crystals had lost some water in the desiccator. Ammonium nitrilosulphonate separates in minute crystals which have only a slight taste, and are somewhat sparingly soluble in water, but so much more so than the potassium salt that E. Frémy suggested that its soln. might be used as a qualitative reagent for potassium salts. It is not volatilized by heat, but is decomposed into sulphate. It is a very unstable salt, being liable in the solid state to decompose (hydrolyze) suddenly with a hissing sound, charring paper in contact with it.

E. Frémy prepared **potassium nitrilotrisulphonate,** $N(KSO_3)_3.2H_2O$, either by mixing soln. of potassium nitrite and sulphite; by rapidly passing a soln. of sulphur dioxide into a dil. soln. of potassium nitrite; or by the action of potassium sulphite on one of the other nitrosulpho-acids salts. A. Claus, and E. Divers and T. Haga showed that E. Frémy must have worked with soln. made alkaline with potassium hydroxide. A. Claus and S. Koch thus describe the process: A soln. of 100 grms. of potassium hydroxide in 200 c.c. of water is neutralized with sulphur dioxide, and mixed with 25 grms. of potassium nitrite in 10 c.c. of water. The mixture very quickly forms a mush of crystals which is allowed to stand for an hour. The alkaline liquid is warmed with the addition of water necessary for the dissolution of the crystals, and allowed to cool. A. Claus and S. Koch believed that if the crystals are separated at once, they consist of *potassium tetrasulphammonate,* $HN(KSO_3)_4$, but this has not been confirmed, and his product is considered to be the impure nitrilotrisulphonate. The slender needles with a pearly lustre were shown by F. Raschig to belong to the rhombic system, and, according to A. Fock, have the axial ratios $a : b : c = 0{\cdot}8156 : 1 : —$. The crystals lose a part of their water over conc. sulphuric acid in vacuo, and all is lost at 100°–110°. At a higher temp., oxygen is given off as well, and potassium sulphate is formed. At a higher temp. still, E. Frémy said that sulphur dioxide, sulphuric acid, and ammonium and potassium sulphates, but no nitrogen oxides are given off. The salt in the course of a month decomposes into hydrosulphate, and imidosulphonate; but F. Raschig, and E. Frémy said that it does not appear to change when kept in an atm. of ammonia. A. Claus and S. Koch said that the salt is insoluble in cold water, and E. Frémy found that at 23°, 100 parts of water dissolve 2 parts of salt. A. Claus and S. Koch said that the salt is not affected by water at 40°, and E. Frémy crystallized the salt by cooling its aq. soln. from 40°–50°. F. Raschig showed that boiling water hydrolyzes the salt to potassium amidosulphonate, and also, if the action has been in progress only a short time, imidosulphonate. The presence of free alkali in the aq. soln. was found by A. Claus to retard the hydrolysis. Dil. acids act like water, but the salt is not decomposed by sulphur dioxide in a cold soln. According to E. Frémy, cold conc. sulphuric acid, and cold nitric acid act slowly, forming potassium and ammonium sulphates. The cold aq. soln. does not precipitate the metal salts, but with warm soln. complex, sparingly-soluble barium and lead salts may be formed. A. Claus and S. Koch said that the soln. in water at 30°–40° gives no precipitate with either baryta-water, or barium chloride; with lead acetate there is a dense, white precipitate of variable composition; mercurous nitrate soln. forms a black powder; and silver nitrate is not changed.

F. Raschig prepared an impure form of **sodium nitrilotrisulphonate,** $N(NaSO_3)_3.5H_2O$, by pouring a conc. soln. of 3 mols of sodium hydrosulphite or pyrosulphite on a mol of solid nitrite avoiding a rise of temp.: $NaNO_2+2Na_2S_2O_5=N(NaSO_3)_3+Na_2SO_3$, but the product also contained hydroxylamino-sulphate, sulphite, and unchanged nitrite were present. E. Divers and T. Haga showed that the soln. should be alkaline, and recommended the following procedure:

A soln. containing 2 mols of sodium nitrate and 3 mols of carbonate and water eq. to about twice the weight of the anhydrous carbonate, is treated with a rapid stream of sulphur dioxide while the soln. is being shaken. The flask is cooled by cold water; and owing to the temporary formation of hydrocarbonate, the shaking is maintained. The warm soln. is now at a temp. of 50°–60°, and the rate of passage of the gas is reduced as the quantity of hydrocarbonate suspended in the soln. lessens. As soon as the soln. reddens litmus, the current of gas is stopped, otherwise the nitrilosulphate will hydrolyze. During the final sulphonation crystals of the nitrilosulphonate separate; and the quantity increases as the soln. cools. It is best to work with the soln. made alkaline by a drop or two of a conc. soln. of sodium hydroxide. The mother-liquor can be evaporated over sulphuric acid for more crystals. The reaction is symbolized: $2NaNO_2+3Na_2CO_3+8SO_2=2N(NaSO_3)_3+Na_2S_2O_5+3CO_2$. The crystals are washed with a little conc. aq. ammonia, and dried on a tile. The excess of pyrosulphite beyond that shown in the equations is necessary for the prompt sulphonation. The crystals containing 21·8 per cent. H_2O lose 15·5 per cent. when dried in vacuo over sulphuric acid.

Sodium nitrilotrisulphate crystallizes in short, thick prisms which melt when heated and decompose in their water of crystallization into sulphates. A. Fock found for the hexagonal prisms the axial ratio $a : c = 1 : 1{\cdot}4413$. E. Divers and T. Haga showed that the crystals cannot be long preserved under any circumstances, soon suffering decomposition and becoming opaque and acid, even in their own liquor after it has been made alkaline. That is, the sodium salt is more unstable than the potassium salt. It is neutral to litmus, and must be soluble in about its own weight of water, to judge from the amount of it left in the mother-liquor in its preparation, although here, no doubt, the pyrosulphite also in soln. will affect its degree of solubility. F. Raschig also reported **sodium dipotassium nitrilotrisulphonate,** $N(SO_3)_3K_2Na$, to be formed by adding a soln. of potassium chloride gradually to a crude soln. of sodium nitrilosulphonate. E. Divers and T. Haga obtained the same salt, which is like the sodium salt in appearance and like the potassium salt in being nearly insoluble. According to F. Raschig, it is anhydrous, and occurs either as a sparkling sand or in hard crystals the size of pinheads and of adamantine lustre.

E. Frémy treated a soln. of barium nitrite with sulphur dioxide and obtained crystals of a salt—probably impure **barium nitrilotrisulphonate,** $\{N(SO_3)_3\}_3Ba_2.nH_2O$ —which gave off ammonia when heated, and which was too unstable to investigate further. E. Frémy also obtained a crystalline precipitate by adding ammonium nitrilosulphonate to a soln. of a barium salt. The composition approximated **ammonium barium nitrilotrisulphonate,** $N(SO_3)_3Ba(NH_4)$. It was sparingly soluble in water; **potassium barium nitrilotrisulphonate,** $N(SO_3)_3BaK.nH_2O$, was made in an analogous way. E. Divers prepared what was possibly **sodium barium nitrilotrisulphonate,** $N(SO_3)_3BaNa.nH_2O$, by adding the sodium salt to a conc. soln. of barium chloride rendered faintly alkaline with ammonia, a flocculent precipitate is obtained which becomes dense and crystalline on standing. It is sparingly soluble in water and very unstable. According to E. Frémy, impure *ammonium lead nitrilosulphonate,* and *potassium lead nitrilosulphonate* have been prepared. F. Ephraim and W. Flügel prepared sparingly soluble **cobalt hexamminonitrilotrisulphonate,** $[Co(NH_3)_6].N(SO_3)_3$; **cobalt aquopentamminonitrilotrisulphonate,** $[Co(NH_3)_5(H_2O)]N(SO_3)_3$; **cobalt cis-dinitritotetramminonitrilotrisulphonate,** $[Co(NH_3)_4(NO_2)_2]N(SO_3)_3$; and **cobalt trans-dinitritotetramminonitrilotrisulphonate,** $[Co(NH_3)_5(NO_2)_2](NSO_3)_3$.

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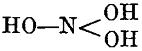
§ 56. Hydronitrilomonosulphonic Acid and its Salts

The sulphazotized acids reported by E. Frémy in his memoir: *Sur une nouvelle série d'acides formés de oxygène, de soufre, d'hydrogène, et d'azote,* (1845), cannot all be identified; but A. Claus' memoir: *Beiträge zur Kenntniss der Schwefelstickstoffsäuren* (1871); F. Raschig's *Ueber das Verhalten der salpetrigen zur schwefligen Säure*

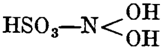
(1887); and E. Divers and T. Haga's *Identification and constitution of Frémy's sulphazotized salts of potassium*, agree more or less closely with the following:

E. Frémy's acids.	Possible equivalents.
Acide sulfazeux, $3SO_2.N_2O_3.3H_2O$	Hydroxynitrilodisulphonic acid
Acide sulfazique, $4SO_2.N_2O_3.3H_2O$	Hydroxynitrilodilsulphonic acid
Acide sulfazotique, $5SO_2.N_2O_3.3H_2O$	Nitritohydroxynitrilodisulphonates
Acide sulfazilique, $4SO_2.N_2O_3.H_2O$	Peroxyamidodisulphonic acid
Acide metasulfazilique, $4SO_2.2SO_3.N_2O_3.3H_2O$	Hydroxynitrilosulphonic acid
Acide sulfazidique, $SO_2.N_2O_3.3H_2O$	Hydroxynitrilomonosulphonic acid
Acide sulfammonique, $8SO_2.N_2O_3.3H_2O$	Nitrilosulphonic acid
Acide metalsulfamidique, $4SO_2.S_2O_2.N_2O_3.3H_2O$	(Transition form)
Acide sulfamidique, $2S_2O_2.N_2O_3.3H_2O$	Imidosulphonic acid

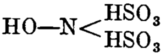
A series of acids can be derived from orthonitrous acid by the substitution of sulphinic, HSO'_2, or sulphonic, HSO'_3, radicles in place of the hydroxyl-groups. The result with the sulphonic radicles is:


$HO{-}N{<}^{OH}_{OH}$

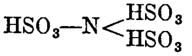
Orthonitrous acid.


$HSO_3{-}N{<}^{OH}_{OH}$

Hydroxynitrilo-monosulphonic acid.

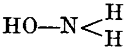

$HO{-}N{<}^{HSO_3}_{HSO_3}$

Hydroxynitrilodisulphonic acid.

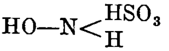

$HSO_3{-}N{<}^{HSO_3}_{HSO_3}$

Nitrilotrisulphonic acid.

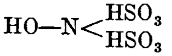
E. Divers and T. Haga [2] obtained no evidence of the existence of the second member of this series; and it was therefore suggested that the series is better regarded as being derived from hydroxylamine by the substitution of sulphonic radicles in place of hydrogen, thus:


$HO{-}N{<}^{H}_{H}$

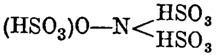
Hydroxylamine.


$HO{-}N{<}^{HSO_3}_{H}$

Hydroxynitrilomono-sulphonic acid.

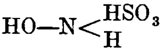

$HO{-}N{<}^{HSO_3}_{HSO_3}$

Hydroxynitrilodisulphonic acid.

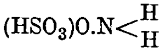

$(HSO_3)O{-}N{<}^{HSO_3}_{HSO_3}$

Hydroxynitrilotrisulphonic acid.

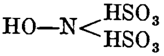
In the case of these mono- and disulphonic acids, isomeric forms are possible.


$HO{-}N{<}^{HSO_3}_{H}$

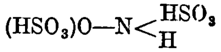
Hydroxynitrilo-monosulphonic acid.


$(HSO_3)O.N{<}^{H}_{H}$

Hydroxynitrilo-iso-monosulphonic acid.


$HO{-}N{<}^{HSO_3}_{HSO_3}$

Hydroxynitrilodi sulphonic acid.


$(HSO_3)O{-}N{<}^{HSO_3}_{H}$

Hydroxynitrilo-iso-disulphonic acid.

According to F. Raschig, the **hydroxynitrilo-iso-monosulphonic acid** appears as a transient intermediate stage in the hydrolysis of the iso-forms of the disulphonates (*q.v.*). It differs from the ordinary form of the monosulphonates in possessing oxidizing properties—*e.g.* it liberates iodine from potassium iodide. He therefore considers this acid as the amide of Caro's acid, **amidopersulphonic acid**, $NH_2.O.HSO_3$. The disulphonic forms will be considered in the next section.

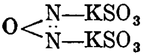
The other acid, **hydroxynitrilomonosulphonic acid**, $HO.NH.HSO_3$, was called *acide sulfazidique* by E. Frémy,[3] and *Sulfhydroxylaminsäure* by A. Claus. It is not known in the solid state; the aq. soln. are fairly stable. E. Frémy, and A. Claus obtained the soln. by decomposing the barium salt with dil. sulphuric acid. F. Raschig represented the reaction between sodium nitrite and hydrosulphite: $NaNO_2+NaHSO_3+SO_2=HO.N(NaSO_3)_2$, and when a soln. of the alkali hydroxynitrilodisulphonate is boiled it decomposes into alkali sulphate and the monosulphonic acid: $HO.N(NaSO_3)_2+H_2O=NaHSO_4+HO.NH.HSO_3$. The former can be precipitated by alcohol, and the evaporation of the filtrate gives a syrupy liquid containing the impure monosulphonic acid. F. Sommer and H. G. Templin obtained the acid of a high degree of purity by the action of chlorosulphonic acid on hydroxylamine hydrochloride at the ordinary temp. It separates from a mixture of ether and methyl alcohol in the form of a microcrystalline powder, liberates iodine from potassium iodide, and is hydrolyzed in acid soln. to hydroxylamine. A soln. of the acid is also obtained by gently warming hydroxylamine sulphate with fuming sulphuric acid. The acid can be purified by dissolving it in cold, dry methyl alcohol and precipitating it with dry chloroform. The hydrolysis of the aq. soln.

of the acid into hydroxylamine and sulphuric acid is accelerated by dil. hydrochloric acid, and by heat: $2(HO)NH(HSO_3)+2H_2O=H_2SO_4+2NH_2OH.H_2SO_4$; the change is completed after many hours' boiling a conc. aq. soln., but in the presence of hydrochloric acid, at 130°, the reaction occupies about an hour. A. Claus, and F. Raschig found the hydrolysis is very rapid in alkaline soln.: $HO.NH.KSO_3+KOH=K_2SO_4+NH_2OH$. Consequently, many of the reactions of the acid are those of hydroxylamine—*e.g.* decoloration with potassium permanganate, evolution of nitrous oxide with sodium nitrite, etc. E. Divers and T. Haga said that in an alkaline soln., the hydrolysis yields a hyponitrite, not hydroxylamine. For other properties, *vide infra* in connection with the salts. A. Angeli showed that with aldehydes, the acid splits into the sulphurous acid and the radicle NOH which immediately combines with the aldehyde to form R.COH : NOH. He therefore considers hydroxynitrilomonosulphonic acid to be related with nitrohydroxylamine, NOH : NO(OH), and he writes the formula $HO.N:SO(OH)_2$. F. Sommer and coworkers found that hydroxynitritomonosulphonic acid reacts with alcohols to form compounds of the type $RO.SO_2.OH,NH_2OH$. Aldehydes and ketones in alkaline soln. react to form salts of oxime acids, *e.g.* $CR_1R_2:NO.SO_2.OK$. On boiling with alkali, the acid is decomposed according to the equation $3NH_2O.SO_2.OH+6KOH=3K_2SO_4+6H_2O+NH_3+N_2$. The salts are very unstable and liable to explode. Many of the reactions of the acid suggest that it possesses the alternative structural formula $HN:O:SO(OH)_2$. On boiling aq. soln. of the acid with a considerable excess of ammonia, 50 per cent. yields of hydrazine are obtained. Amino-compounds yield the corresponding hydrazine derivatives. Alkaline soln. of ethylenediamine react to form *a-hydrazino-β-aminoethane*, which furnishes a number of salts. Benzylidene-hydrazino-β-aminoethane was also obtained.

According to A. P. Sabanéeff, **ammonium hydroxynitrilomonosulphonate,** $HO.NH.NH_4SO_3$, is obtained by boiling a soln. of the potassium salt for a few minutes, and adding barium hydroxide to the filtered liquid whereby barium hydroxynitrilomonosulphonate is precipitated. This salt is decomposed with ammonium sulphate. The crystals decompose on keeping. The salt is isomeric with hydroxylamine amidosulphonate, $NH_3OH.NH_2.SO_3$, and with hydrazine sulphate, $N_2H_4.H_2SO_4$. E. Frémy made **potassium hydroxynitrilomonosulphonate,** $HO.NH.KSO_3$, which he called *sulfazidate de potasse*, along with potassium hydrosulphate by boiling a soln. of the corresponding disulphonate in water, or allowing the soln. to stand for some time.

The aq. soln. of potassium hydroxynitrilodisulphonate is boiled for some minutes, neutralized with ammonia, treated with barium chloride, and filtered. The clear liquor is treated with baryta-water when barium hydroxynitrilomonosulphonate is precipitated. The product is treated with dil. sulphuric acid, and the aq. soln. of the acid neutralized with potassium hydroxide, and the soln. evaporated for crystallization.

The hexagonal plates so obtained have a neutral reaction. They decompose when heated, forming oxygen, ammonia, and potassium hydrosulphate, and the same products were reported by E. Frémy to be formed when the salt is boiled with alkali-lye, while, according to A. Claus, one-third to one-half the nitrogen is thus given off as ammonia, and the remainder as nitrous oxide. A. Claus said that the aq. soln. mixed with a cold soln. of potassium hydroxide has the characteristics of a soln. of hydroxylamine, but E. Divers and T. Haga showed that a sulphite and hyponitrite, not hydroxylamine, are produced: $HO.NH.KSO_3+2KOH=KO.NK.KSO_3+2H_2O$, followed by $2(KO.NK.KSO_3)=K_2N_2O_2+2K_2SO_3$. Ammonia is not formed, and very little sulphate or nitrogen appears. If the aq. soln. of the salt be evaporated with sodium carbonate, carbon dioxide is evolved, and sodium hyponitrite is formed. According to A. Claus, dil. acids or water decomposed the salt with prolonged boiling, the action is slow because the salt can be crystallized from boiling water, or by evaporating the aq. soln. The products of the decomposition by dil. acids are ammonia, sulphuric acid, oxygen, and nitrous oxide. E. Divers and T. Haga said that the aq. soln. reduces salts of silver and gold, while with copper salts, the decomposition can be symbolized: $2(HO.NH.KSO_3)+2CuO+2KOH=K_2SO_3+K_2SO_4+Cu_2O+N_2O+3H_2O$. E. Frémy said that the warm aq. soln. reacts with manganese dioxide giving off oxygen. The salt is not soluble in alcohol. According to F. Raschig, the salt is oxidized by iodine: $2(HO.NH.KSO_3)+2I_2+H_2O=N_2O+4HI+2KHSO_4$. The primary product of the oxidation in alkaline soln. is to form the residue, $(OH).N.KSO_3$, which, by condensation, forms $KSO_3.N(OH).N(OH).KSO_3$, a product which loses water, forming oxydiazodisulphonate:



$$O<\begin{matrix}N—KSO_3\\ \ddot{N}—KSO_3\end{matrix}$$

This is unstable and yields half its sulphur as sulphite and the remainder as a dinitrosulphonate, $K_2N_2O_2.SO_3$.

E. Frémy, and E. Divers and T. Haga prepared **sodium hydroxynitrilomonosulphonate** as a clear, gummy, viscid, neutral liquid, which did not solidify or show any signs of crystallization. E. Frémy reported **dibarium hydroxynitrilomonosulphate,** as *sulfazidate de baryte*, and A. Claus as *sulfhydroxylaminsaures Baryum*. The mode of preparation, used by E. Frémy, and by E. Divers and T. Haga, is indicated above in connection with the ammonium and potassium salts. The white crystalline precipitate is sparingly soluble in water; and the soln. has an alkaline reaction. It is soluble in hydrochloric acid, and when heated, it detonates with the production of ammonia and oxygen. E. Divers and T. Haga also made **barium hydroxynitrilomonosulphonate,** $(HO.NH.SO_3)_2Ba.H_2O$, by adding to the dibarium salt as much sulphuric acid as is necessary to precipitate half the barium as barium sulphate, and evaporating the neutral filtrate over conc. sulphuric acid. The crystals are tabular and prismatic and very soluble in water; they decompose on keeping; and when heated to 100°, decompose suddenly into gases and barium sulphate. W. Flügel prepared **cobalt hexamminodihydroxynitrilomonosulphonate,** $[Co(NH_3)_6]\{(HO)_2N(SO_3)\}_2$, freely soluble in water.

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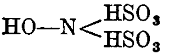
[2] F. Raschig, *Ber.*, 39. 245, 1906; *Schwefel- und Stickstoffstudien*, Leipzig, 132, 1924; E. Divers and T. Haga, *Journ. Chem. Soc.*, 77. 437, 1900.

[3] E. Divers and T. Haga, *Journ. Chem. Soc.*, 55. 766, 1889; E. Frémy, *Ann. Chim. Phys.*, (3), 15. 446, 1845; A. Claus, *Liebig's Ann.*, 158. 85, 1871; F. Raschig, *ib.*, 241. 185, 1887; *Schwefel- und Stickstoffstudien*, Leipzig, 154, 1924; A. Angeli, *Atti Accad. Lincei*, (5), 10. ii, 158, 1901; A. P. Sabanéeff, *Zeit. anorg. Chem.*, 17. 480, 1898; F. Sommer, O. F. Schulz, and M. Nassau, *ib.*, 147. 142, 1925; F. Sommer and H. G. Templin, *Ber.*, 47. 1221, 1914; W. Flügel, *Jahrb. Phil. Fakultät. Bern*, 4. 84, 1924; F. Ephraim and W. Flügel, *Helvetica Chim. Acta*, 7. 724, 1924.

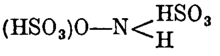
§ 57. Nitrilohydroxydisulphonic Acid and its Salts

As indicated in the preceding section, there are two isomeric forms of these acids:



$$HO—N<\begin{matrix}HSO_3\\ HSO_3\end{matrix}$$

Normal acid.



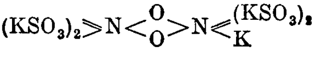
$$(HSO_3)O—N<\begin{matrix}HSO_3\\ H\end{matrix}$$

Iso-acid.

F. Raschig[1] prepared salts of what he called *hydroxylaminodisulphonic acid;* and E. Divers and T. Haga salts of what they called *oximidosulphonic acid*, which is here regarded as a nitrilosulphonic acid with one sulphonic radicle replaced by an hydroxyl-group. It is hence called **nitrilohydroxydisulphonic acid,** or **hydroxynitrilodisulphonic acid,** $N(OH)(HSO_3)_2$. E. Divers, and W. C. Reynolds and W. H. Taylor showed that the acid is formed as an intermediate stage in the reaction between nitrous and sulphurous acids because, working at 0°, if one mol. proportion of the former is mixed with two of the latter the reaction: $HNO_2+2H_2SO_3=H_2O+(HO)N(HSO_3)_2$, takes place, and if the product is neutralized and concentrated, alkali hydroxynitrilodisulphonate is formed. On the other hand, the product of the interaction of the two acids furnishes nitrous oxide if mixed with another mol of nitrous acid: $(HO)N(HSO_3)_2+HNO_2=N_2O+2H_2SO_4$—*vide infra*, nitrosyl sulphonic acid. The oxidation products of hydroxynitrilosulphonic acid in acid and alkaline soln. are the same: $2(HO)N(HSO_3)_2+O=2NO+2H_2SO_4+H_2O$, but in alkaline soln. the nitric oxide combines with the sulphite to form alkali hyponitritosulphate—*vide infra.* Hydroxynitrilodisulphonic acid itself has not been isolated, but numerous salts have been reported. In the so-called neutral salts, only the hydrogen atoms of the hydroxyl group of the acid radicle are replaced by a metal, M′, forming the series $HO.N(MSO_3)_2$; and in the so-called basic salts all the hydrogen atoms are displaced by the metal, forming $MO.N(MSO_3)_2$. There are also complex salts formed by the union of the basic and neutral salts. This makes the subject somewhat complex. The most important memoir on the subject is E. Divers and T. Haga's *Oximidosulphonates or Sulphazotates.* E. Frémy described a number of these salts, and the subject was also examined by A. Claus. F. Raschig said that hydroxynitrilodisulphonic acid in a cold acid soln. yields the monosulphonic acid; and when the alkali salt is oxidized with a dil. soln. of permanganate, what he called *sodium sulphazalinate*, $O:N:(NaSO_3)_2$, is formed, and this, when hydrolyzed with potassium hydroxide furnishes the di- and tri-sulphonates: $4NO(KSO_3)_2+KOH=KNO_2+2NO(KSO_3)_3+HO.N(KSO_3)_2$. F. Raschig said that **potassium iso-hydroxynitrilodisulphonate,** $NH(KSO_3).O.KSO_3$, is produced by the hydrolysis of the corresponding trisulphonate with a weak acid. In the presence of hydrochloric acid, the KSO_3-group attached to the nitrogen atom may be eliminated to form *iso*-hydroxynitrilomonosulphonic acid, $NH_2.O.HSO_3$. The reaction of the *iso*-disulphonate with hypochlorite is represented: $KSO_3.NH.O.KSO_3+3NaOCl+H_2O=HNO_3+2KHSO_4+3NaCl$; and with permanganate soln., the *iso*-monosulphonate is formed, then $NO.HSO_4$, and finally nitrous oxide and sulphate.

E. Divers and T. Haga prepared **triammonium hydroxynitrilodisulphonate,** $NH_4O.N(NH_4SO_3)_2$, by shaking the basic lead salt with a soln. of ammonium hydrocarbonate, or the barium salt with a soln. of normal ammonium carbonate. The salt could not be isolated, because, when the clear soln. is conc. by evaporation in air, it decomposes with the evolution of ammonia. If the soln. be mixed with conc. ammonia, and evaporated in an atm. of ammonia over potassium hydroxide, prismatic crystals form as a crust near the walls of the containing vessel. They slowly effloresce in dry air. The analytical results were not satisfactory; it is possibly a complex salt—*pentammonium hydroxybisnitrilodisulphonate*—or solid soln. of a mol each of $HO.N(SO_3NH_4)_2$ and $NH_4O.N(SO_3NH_4)_2$, If the aq. soln. of the triammonium salt be evaporated to a small volume keeping the soln. alkaline by adding a drop of ammonia from time to time, and finishing the evaporation rapidly over sulphuric acid, prismatic crystals of **diammonium hydroxynitrilodisulphonate,** $HO.N(NH_4SO_3)_2$, are formed. All three ammonium salts are decomposed when heated with the formation of ammonium hydrosulphate.

F. Raschig prepared **tripotassium hydroxynitrilodisulphonate,** $KO.N(KSO_3)_2.H_2O$, which he called *basic potassium sulphazotate*, by rapidly cooling a hot aq. soln. of the dipotassium salt and adding a cold soln. of potassium hydroxide until the liquid begins to appear turbid; or adding an excess of potassium hydroxide to a warm soln. of the pentapotassium salt, and then adding alcohol. E. Divers and T. Haga obtained the salt in an analogous way—the precipitate obtained with alcohol was the dihydrated salt. F. Raschig assumed that the salt is bimolecular and has the constitution:



$$(KSO_3)_2{\geqslant}N{<}{}^{O}_{O}{>}N{\leqslant}{}^{(KSO_3)}_{K},$$

It forms needle-like crystals, or a crystalline powder; when recrystallized from water, it forms the dipotassium salt. It decomposes when heated with explosive violence. It is freely soluble in cold water, and reacts towards salts of the heavy metals like free alkali, forming at the same time a soln. of the dipotassium salt. E. Divers and T. Haga reported a complex salt with potassium nitrite—**tripotassium nitritohydroxynitrilodisulphonate,** $2(KO)N(KSO_3)_2.KNO_2$, with $4{\cdot}4H_2O$, and $6H_2O$. The potassium metasulphazotinate of E. Frémy is supposed by F. Raschig to be the impure dipotassium salt, and by E. Divers and T. Haga to be a mixture of the normal tripotassium salt with the complex of that salt and potassium nitrite.

E. Frémy described what he called *sulfazotate de potasse basique;* A. Claus, *potassium sulphazotate;* and F. Raschig, *neutral potassium sulphazotate,* which E. Divers and T. Haga showed to be **pentapotassium hydroxybisnitrilodisulphonate,** $HO.N(KSO_3)_2.KO.N(KSO_3)_2.H_2O$. E. Divers and T. Haga showed that this is only one way of preparing this salt, namely, by dissolving the dipotassium salt in a soln. of enough potassium hydroxide or an eq. salt, and crystallizing. The dipotassium salt should not be put into cold water, or even into the alkali-lye, and then heated for its dissolution unless the mixture is continuously stirred; otherwise, undissolved salt lying on the bottom of the vessel is liable to hydrolysis. This method was used by A. Claus, and F. Raschig. In E. Frémy's process, the salt is apparently formed direct by sulphonating the nitrite, but in reality, the dipotassium salt is first formed, and then converted by the alkali-lye into the five-sixths salt. E. Frémy said the crystals are white, rhombic columns; A. Claus, rhombohedral crystals, which, when rapidly formed, furnish aggregates *en tremies.* They have an alkaline reaction and caustic taste. The crystals were said to lose no water at 120°, but E. Divers and T. Haga found that water is given off slowly at this temp., and that the water is restored by exposure to the atm. A. Claus said that the crystals can be preserved for months without change, but not if any of the dipotassium salt be present. E. Frémy showed that the crystals become matt at 140°–160°, give off red fumes, sulphur dioxide, and ammonium sulphite, leaving a residue of potassium sulphite; the salt decomposes slowly when boiled with water; and A. Claus said that it loses potassium when repeatedly crystallized from water. E. Frémy showed that the salt is not soluble in alcohol or ether; and found that red fumes are evolved when the salt is treated with nitric acid, and, added A. Claus, the whole of the sulphur is transformed into sulphuric acid. E. Frémy, and A. Claus showed that conc. sulphuric acid decomposes the salt with the evolution of nitric oxide. If the aq. soln. be warmed with silver oxide, lead dioxide, or chlorine, it acquires a violet colour, and is transformed into potassium nitroxysulphonate. A. Claus showed that one-third of the nitrogen is given off as ammonia when the salt is heated with admixed soda-lime. Almost all salts of the metals—excepting those of calcium and strontium—give precipitates of variable composition when their soln. are treated with this salt.

F. Raschig claimed to have made an isomeric form of this salt—which he called *potassium hydroxylamineisodisulphonate*—but E. Divers and T. Haga believed that the alleged isomer was a complex salt of potassium nitrite and the dipotassium salt. F. Raschig recommended the following process for making the potassium salt: sodium hydrosulphite soln. (5*N*-, 1200 c.c.) is added with continuous stirring to a mixture of ice (1000 grms.) and commercial sodium nitrite (150 grms.), whereby the temp. is not allowed to rise above 5°. One c.c. of the soln., when tested after the addition has been finished for ten minutes, should react with about 17 c.c. of 0·1*N*-iodine soln., and subsequently require 14–15 c.c. of 0·1*N*-sodium hydroxide for neutralization in the presence of methyl-orange. Any ice particles are removed and the soln. is treated whilst being vigorously shaken with lead dioxide (600 grms.). It is subsequently warmed on the water-bath, frequent agitation being required to prevent the oxidizing agent from becoming aggregated. The conclusion of the oxidation is reached when 1 c.c. of the soln. neutralizes about 9 c.c. of 0·1*N*-hydrochloric acid and subsequently does not react with more than 1 c.c. of 0·1*N*-iodine soln. The soln. is filtered and the residue washed with hot water (200 c.c.). The filtrate is warmed with commercial potassium chloride (800 grms.) until the precipitated lead chloride forms coarse particles, which are removed. The filtrate, after remaining for three days in an ice-chest, deposits potassium hydroxylaminetrisulphonate (790 grms.) in large mono-symmetric prisms. It is filtered, dried on porous earthenware, and subsequently over calcium chloride. The finely-divided, dry salt (423 grms.) is agitated with boiling water (800 c.c.) containing 1 c.c. of dil. hydrochloric acid until soln. is complete; the small amount of lead sulphate which separates is removed. The filtrate deposits potassium hydroxylamineisodisulphonate in colourless crystals, the yield being about 90 per cent. of that theoretically possible. E. Divers and T. Haga made three complex salts with potassium nitrate—pentapotassium nitritohydroxylnitrilodisulphonate—namely, $2K_5H(NS_2O_7).7KNO_2.3H_2O$; $K_5H(NS_2O_7).3K_2NO_2.H_2O$; and $3K_5H(NS_2O_7).7KNO_2$. E. Divers showed that the *sulfazinate de potasse* of E. Frémy, and A. Claus is a mixture of one of these complex salts with the tri- and di-potassium salts; and the *metasulfazate de potasse* of E. Frémy, a mixture of the tripotassium salt and one of the complex salts with potassium nitrite.

The sulfazotate de potasse neutre of E. Frémy, the *disulfhydroxyazosaures Kalium* of A. Claus, and the *potassium oximidosulphonate* of E. Divers and T. Haga, is **dipotassium hydroxynitrilodisulphonate,** $HO.N(KSO_3)_2.2H_2O$. E. Frémy prepared this salt by passing sulphur dioxide into a soln. of potassium nitrite and hydroxide. If the soln. be too conc., the tri-potassium salt is formed, in that case water is added to dissolve the salts and the current of gas continued. A. Claus always obtained some nitrilosulphonate when using this process, but by keeping the soln. cool during the passage of the gas, he obtained a soln. which gave crystals of the dipotassium salt on standing. F. Raschig did not obtain good results with this process. E. Divers and T. Haga speak very highly of this mode of preparing both the disodium and dipotassium salts. The former salt may be taken as a type for both:

Fifty grms. of sodium nitrite containing 96 per cent. $NaNO_2$ and 100 grms. of sodium carbonate (or 30·8 grms. of sodium hydroxide) are mixed with 150 c.c. of water in a 500 c.c. flask (if sodium hydroxide is used, 200 c.c. of water are needed). A piece of lacmoid paper is also placed in the flask. A rapid stream of sulphur dioxide is passed through the soln. while the containing flask is agitated, and cooled in a freezing mixture. In about 70 minutes, the soln. will be acidic to lacmoid paper. The nitrilosulphonate which is present is hydrolyzed into imidosulphonate and hydrosulphonate, and to make sure that this change is completed, the well-cooled soln. is left in its acidic condition for 10–15 minutes. The sulphur dioxide is removed by a stream of air. A conc. soln. of sodium carbonate is now added until the soln. is alkaline. This prevents the hydrolysis of the disodium salt. The soln. now contains about 150 grms. of the disodium salt, 15 grms. imidosulphonate, and 22 grms. of sodium sulphate in about 220 c.c. of water. The filtered soln. is evaporated either at a gentle heat in air, or in vacuo over sulphuric acid. When the soln. weighs about 300 grms., it is cooled in ice, and after some hours it is strained free from the crystals of sodium sulphate. When the soln. is further conc. in vacuo, a crop of crystals of the disodium salt appears, and when 90–100 grms. has separated, the soln. may be again cooled to crystallize out more sodium sulphate. Another evaporation gives another crop of crystals of the disodium salt. The salt may be recrystallized from a small quantity of hot water rendered alkaline with ammonia. The main reaction is represented $NaNO_2+NaOH+2SO_2=HO.N(NaSO_3)_2$.

F. Raschig mixed a mol of potassium nitrite dissolved in as little water as possible with a well-cooled soln. of 2 mols of potassium hydrosulphite, and added a cold sat. soln. of about 2 mols of potassium chloride. In 24 hrs., the needle-like crystals of nitrilosulphonate were separated from the crystalline crust of the nitrilodisulphonate by washing. The latter salt can be purified by crystallization from warm water rendered alkaline by ammonia or potassium hydroxide. A. Claus also made the salt by mixing 4 mols of potassium sulphite and one of potassium nitrite. The soln. is filtered from the crystals of nitrilosulphonate, and in about 10–12 hrs. it deposits crystals of dipotassium nitrilodisulphonate. He also made the same salt by crystallization from a soln. of potassium nitrosyl sulphonate in warm water.

The well-defined, colourless, prismatic crystals of dipotassium nitrilodisulphonate were found by A. Fock to belong to the monoclinic system, and to have the axial ratios $a:b:c=1·5490:1:0·9208$, and $\beta=74°$. The crystals, said E. Frémy, are neutral and nearly tasteless. A. Claus said that the crystals are stable only when in the presence of free alkali; if treated with water free from alkali, the crystals decomposed in half an hour when confined over sulphuric acid in vacuo. F. Raschig also said that the salt decomposes in a few days when confined in an atm. of ammonia, forming nitrilomonosulphonate and sulphate. The hydrolysis occurs very rapidly in acidic soln. The crystals detonate when heated rapidly to about 85°, and when slowly heated, water is given off. E. Divers and T. Haga found that when heated to 170°–180° in moist air, water is absorbed and hydrolyzes the salt. When the dehydrated crystals are heated above 100°, acid vapours are given off along with sulphur dioxides; the salt melts and forms ammonium and potassium sulphates and free sulphuric acid. Conc. nitric acid acts on the crystals, giving off red fumes and transforming the sulphur into sulphuric acid. A. Claus said that when heated with soda-lime, one-third of the total nitrogen is given off as ammonia. Barium salts with warm soln. give a precipitate of barium sulphate; while lead and silver salts give no precipitation. According to E. Divers and T. Haga, when boiled with a soln. of copper sulphate, a copper salt is formed which is partly oxidized and partly reduced, forming nitrous oxide, water, sulphuric acid, and copper sulphate. They also prepared a complex salt with potassium nitrate, **dipotassium nitratohydroxynitrilodisulphonate,** $HO.N(KSO_3)_2.KNO_3.H_2O$; with sodium chloride, **decapotassium octosodium chlorohydroxynitrilodisulphonate,** $5(HO)N(KSO_3)_2.8NaCl.3H_2O$; and with potassium nitrite, **dipotassium nitritohydroxynitrilosulphonate,** $HO.N(KSO_3)_2.KNO_2$; they say that F. Raschig's *sulfazinsaure Kalium* is the same as the complex salt with potassium nitrate; and similarly also with his *basisch dihydroxylaminsulfosaure Kalium.* This is also the case with E. Frémy's *sulfazite de potasse.*

E. Divers and T. Haga prepared **trisodium hydroxynitrilodisulphonate,** by adding the calculated quantity of sodium hydroxide to a soln. of the disodium salt and evaporating for crystallization; or it is precipitated from a conc. soln. of the disodium salt by adding an excess of sodium hydroxide. The rhombic, prismatic crystals begin to decompose when heated in air to 100°, owing to the action of the absorbed moisture; if moist air be excluded, they decompose at 182°–183°, forming a residue of sodium sulphate and thiosulphate, a little sublimate of sulphur and an ammonium salt, and the gases sulphur dioxide and nitrogen: $2NaO.N(NaSO_3)_2=3Na_2SO_4+N_2+SO_2$. At 20°, 100 parts of water dissolve 77 parts of the salt; the soln. is strongly acidic, and inclined to supersaturation. The soln. reacts towards metal salt soln. like free alkali-lye, and the disodium salt passes into soln. If a soln. of the disodium salt be mixed with some sodium hydroxide, or the trisodium salt; or a soln. with the theoretical proportions of the component salts be evaporated in a desiccator, prismatic or tabular crystals of what is probably the *pentasodium hydroxybisnitrilodisulphonate* are formed; but on filtration the crystals are those of **octosodium hydroxytrisnitrilodisulphonate,** $HO.N(NaSO_3)_2.2(NaO)N(NaSO_3)_2.3H_2O$. When recrystallized from water, microscopic crystals are formed without decomposition. At 14°, 100 parts of water dissolve 66 parts of the salt. The aq. soln. is easily supersaturated. E. Divers and T. Haga also prepared **disodium hydroxynitrilodisulphonate,** $HO.N(NaSO_3)_2$, by the process indicated above. The salt appears in thick prismatic crystals which can be recrystallized without chemical change from ammoniacal water. The salt is decomposed by the moisture in atm. air, but in dry air it can be heated slowly to 140°, and rapidly to 171°, whereby the salt fuses and decomposes with intumescence. The residue consists of sodium hydrosulphate, and the gases which are formed consist of sulphur dioxide and nitrogen. No nitrous fumes were observed; but some nitrous fumes are given off when the salt is treated with sulphuric acid. The salt is soluble in rather more than its own weight of water, and the soln. reddens blue litmus. The trisodium salt is formed when the aq. soln. is evaporated with sodium acetate or carbonate. 100 c.c. of a sat. soln. of sodium chloride dissolve 25 grms. of the salt, and from the soln. a complex salt is precipitated. It forms complex salts with potassium nitrate, but not with potassium chloride, or sodium nitrate or sulphate. It also forms a complex salt with sodium nitrite, **disodium nitritohydroxynitrilodisulphonate,** $HO.N(NaSO_3)_2.NaNO_2$, which on account of its free solubility was not investigated closely.

E. Divers and T. Haga prepared a number of complexes, **potassium sodium hydroxynitrilodisulphonates.** There is nothing to show which of the complexes in the following list are chemical individuals: $3K_3(NS_2O_7).2Na_3(NS_2O_7).1\frac{1}{2}H_2O$; $6K_3(NS_2O_7).Na_3(NS_2O_7).H_3(NS_2O_7).20H_2O$; $K_2H(NS_2O_7).2Na_2H(NS_2O_7).4Na_3(NS_2O_7).5H_2O$; $KNaH(NS_2O_7).Na_3(NS_2O_7)$; $K_{1\cdot4}Na_{1\cdot6}(NS_2O_7).H_2O$; $5K_3(NS_2O_7).Na_3(NS_2O_7).Na_2H(N_2O_7).H_3(NS_2O_7).9H_2O$; $K_{2\cdot1}Na_{0\cdot3}H_{0\cdot6}(NS_2O_7).0\cdot72H_2O$; $K_{3\cdot75}NaH_{1\cdot25}(NS_2O_7)_2.18H_2O$; $K_3(NS_2O_7).KNaH(NS_2O_7)$; $2K_3(NS_2O_7).NaH_2(NS_2O_7).2H_2O$; $KNaH(NS_2O_7).3H_2O$.

Barium chloride does not give a precipitate with a soln. of the dipotassium or disodium salt, but the mixed soln. are very unstable, and, as shown by A. Claus, rapidly hydrolyze, forming the sulphate and hydroxynitrilosulphonate. E. Divers and T. Haga prepared **tribarium hydroxynitrilodisulphonate,** $Ba_3(NS_2O_7)_2.4H_2O$ (and $8H_2O$), by the action of barium chloride or hydroxide on an excess of a soln. of the trisodium salt; the washed precipitate is nearly all dissolved in dil. hydrochloric acid until a neutral soln. or one slightly alkaline to litmus is formed; the turbid soln. is rapidly filtered into an excess of warm baryta-water; and the precipitate washed with well-boiled hot or cold water. The voluminous, curdy precipitate generally changes to a chalk-like powder consisting of crystalline particles. It is practically insoluble in water, but soluble in a soln. of ammonium chloride. It is decomposed in the cold by soln. of ammonium or sodium carbonate. If heated dry, it suddenly decomposes into barium sulphate and gases; it loses water at ordinary temp., in dry air, and nearly all at 110°. A soln. of **barium hydroxynitrilodisulphonate,** $HO.N(SO_3)_2Ba$, can be obtained by adding just enough sulphuric acid to the tribarium salt, and filtering. The soln. is acid to litmus, and hydrolyzes too quickly to permit the isolation of the salt. A compound $(HOBa)_2HNS_2O_7$, or $(HOBa)Ba.NS_2O_7$, is known only in combination.

E. Divers and T. Haga prepared a series of **potassium barium hydroxynitrilodisulphonates;** *e.g.* $4KBa(NS_2O_7).(HOBa)_2H(NS_2O_7).H_2O$; $K_2H(NS_2O_7)K_3(NS_2O_7)$; $3Ba(OH)_2.K_3(NS_2O_7).3Ba_3(NS_2O_7)$; $KBa(NS_2O_7).H_2O$; $K_3(NS_2O_7).3Ba_3(NS_2O_7)_2.14H_2O$; and $Ba_3(NS_2O_7)_2.4K_2H(NS_2O_7).9H_2O$; as well as $BaCl_2.2Ba(OH)_2.4Ba_3(NS_2O_7)_2.2K_3(NS_2O_7).14H_2O$. They also prepared a series of **sodium barium hydroxynitrilodisulphonates,** *e.g.* $5Na(NS_2O_7).6Ba_3(NS_2O_7)_2.24H_2O$; $Na_3(NS_2O_7).2Ba_3(NS_2O_7)_2.7H_2O$; and $Na_3(NS_2O_7).3Ba_3(NS_2O_7)_2.7H_2O$.

Neither E. Frémy, nor A. Claus obtained a precipitate on adding an alkali hydroxynitrilodisulphonate to a strontium salt, but E. Divers and T. Haga showed that the soln. remains clear for a moment, then forms a voluminous silky precipitate; while with the ammonium or potassium salts, the soln. deposits silky crystals in a few hours. The **potassium strontium hydroxynitrilodisulphonate** had the composition $(HOSr)_3(NS_2O_7).8SrK(NS_2O_7).16H_2O$; while the **sodium strontium hydroxynitrilodisulphonate** and the **ammonium strontium hydroxynitrilodisulphonate** were not analyzed. E. Frémy obtained needle-like crystals by the action of sulphur dioxide on a soln. of calcium nitrite; they gave off ammonia when heated, but were not further examined. According to E. Divers and T. Haga, calcium salts give no precipitate with soln. of the alkali hydroxynitrilodisulphonates, but the hydroxide forms salts by reacting with ammonium hydroxynitrilodisulphonate, mol for mol. The evaporation of the soln. on the water-bath gives off ammonia and forms a crystalline residue, probably **ammonium calcium hydroxynitrilodisulphonate,** $Ca(NH_4)(NS_2O_7)$, or **calcium hydroxynitrilodisulphonate,** $CaHNS_2O_7$. If this is treated with water, some nearly insoluble calcium hydroxynitrilodisulphonate is left, but the greater part dissolves as the calcium ammonium salt. If after dissolving 2 mols of calcium hydroxide in 2 mols of the ammonium salt, a third mol of the softest moist calcium hydroxide be stirred in, it is converted into a voluminous precipitate, which most probably is normal **calcium hydroxynitrilodisulphonate;** this precipitate is only sparingly soluble in water, and is so free from ammonia as to evolve none when mixed with calcium hydroxide, a test, however, which is not quite conclusive.

According to E. Divers and T. Haga, the reactions of the alkali hydroxynitrilodisulphonates with lead salts are complex; the disodium and dipotassium salts give no precipitates with normal lead acetate, but they do so with soln. of basic lead acetate. Trisodium hydroxynitrilodisulphonate and normal lead acetate give no precipitate unless the soln. are dil., but with basic lead acetate there is no precipitate unless the lead salt is in excess. The tripotassium salt gives an immediate precipitate with normal lead acetate, but with conc. soln. and basic lead acetate the clear soln. deposits a flocculent precipitate, which dissolves on heating and re-deposits on cooling. If basic lead acetate in excess be treated with the trisodium salt, the voluminous flocculent precipitate, when washed and dried, is **triplumbhydroxyl hydroxynitrilodisulphonate,** $(PbOH)_3NS_2O_7.3H_2O$. The reaction is symbolized $Na_3(NS_2O_7)+3(PbOH)C_2H_3O_2=(PbOH)_3(NS_2O_7)+3NaC_2H_3O_2$; the same salt is formed by adding the disodium salt to an excess of highly basic lead acetate, $Na_2H(NS_2O_7)+Pb_3(OH)_4(C_2H_3O_2)_2=2NaC_2H_3O_2+H_2O+(PbOH)_3(NS_2O_7)$. The salt decomposes when heated to a moderate temp.: $(PbOH)_3(NS_2O_7)=HO.PbNO_2+2PbSO_3+H_2O$; and the residue, when heated still more, gives off red fumes; and if moistened with hydrochloric or sulphuric acid, evolves sulphur dioxide. The salt is insoluble in acetic and other acids, and in soln. of ammonium chloride or other ammonium salts, and sodium hydroxide. It is immediately and completely dissolved by cold soln. of sodium, potassium, or ammonium hydrocarbonate. When the salt is stirred with enough sulphuric acid to deprive it of two-thirds of its lead, the slightly acid mother-liquid, on evaporation in a desiccator, gives a crust of minute crystals which, under the microscope, appear as transparent prisms. The salt was not analyzed, but was thought to be **lead hydroxynitrilodisulphonate,** $PbH(NS_2O_7)$. If basic lead acetate be added to a slight excess of the dipotassium salt, **diplumbhydroxyl hydroxynitrilodisulphonate,** $(PbOH)_2H(NS_2O_7).H_2O$, is formed as a voluminous flocculent precipitate, $K_2H(NS_2O_7)+2(PbOH)C_2H_3O_2=2KC_2H_3O_2+(PbOH)_2H(NS_2O_7)$.

A complex salt with lead acetate was also prepared, *viz.*, **tetraplumbhydroxyl acetobishydroxynitrilodisulphonate,** $(PbC_2H_3O_2)(PbOH)_4H(NS_2O_7)_2.2\frac{1}{2}H_2O$; and a couple of **potassium lead hydroxynitrilosulphonates**: $(PbOH)_5K_5H_2(NS_2O_7)_4$; and $(PbOH)PbK_6(NS_2O_7)_3$. A salt similar to the latter was reported by F. Frémy. E. Divers and T. Haga also reported **sodium lead hydroxynitrilosulphonate,** $(PbOH)_2Na_6H(NS_2O_7)_3.14H_2O$; and **ammonium lead hydroxynitrilosulphonate,** $(PbOH)NH_4(NS_2O_7)$. The disodium and dipotassium hydroxy-lead salts cannot be prepared in a similar way, but a soln. of either of these salts, or of the diammonium salt, along with acetate, seems to be obtained on mixing conc. soln. containing basic lead acetate and the trisodium, tripotassium, or triammonium salts in mol. proportion. The soln. dries up to a vitreous mass, with a little crystalline matter, and is precipitated on dilution with water.

T. Haga[2] discovered salts of **hydroxynitrilo-iso-disulphonic acid,** $HSO_3.O:NH.HSO_3$, which F. Raschig called *Hydroxylamin-iso-disulfonsäure*, and T. Haga, *hydroxylamin-αβ-disulphonic acid*. The acid is dibasic, and forms a series of salts, the **hydroxynitrilo-iso-disulphonates.** Unlike the hydroxylnitrilodisulphonates, T. Haga showed that (i) the iso-salts furnish the sulphate and the amidosulphonate: $H_2O+2Na+(NaSO_3)O.NH.NaSO_3=Na_2SO_4+NaOH+(NH_2)SO_3Na$, while the ordinary salt is unaffected; (ii) while the ordinary salt reverts to nitrite and sulphite when it is left, even in the cold, in a conc. soln. of potassium hydroxide: $HO.N(KSO_3)_2+3KOH=KNO_2+2H_2O+2K_2SO_3$, the iso-salt is incompletely decomposed into sulphate, amidosulphonate, and nitrogen after many hours' digestion at 100°–125°: $3\{(KSO_3)O.NH.KSO_3\}+5KOH=5K_2SO_4+N_2+3H_2O+NH_2.KSO_3$; and (iii) the aq. soln. of the iso-salt is not coloured bluish-violet when treated with lead dioxide, or silver oxide, whereas the aq. soln. of the ordinary salt gives a coloration. F. Raschig also showed that (iv) the iso-salt is not hydrolyzed so readily as the ordinary salt; and (v) whilst the potassium iso-salt separates from hot acidified soln. in anhydrous crystals, those of the ordinary salt are dihydrated.

T. Haga prepared **diammonium hydroxynitrilo-iso-disulphonate,**

$NH_4SO_3O.NH.NH_4SO_3$, by crystallizing ammonium hydroxynitrilotrisulphonate from its soln. in hot water, acidified with a drop of sulphuric acid. The trisulphonate is hydrolyzed into a sulphate and the iso-sulphonate: $2\{(NH_4SO_3)O.N(NH_4SO_3)_2\} + 2H_2O = 2\{(NH_4SO_3)O.NH.NH_4SO_3\} + 2NH_4(HSO_4)$. The hydrosulphate is eliminated by adding just enough baryta-water, filtering, and evaporating, at first at a gentle heat and then in the cold, over sulphuric acid under reduced press. It occurs as small, thick plates, which are somewhat hard, and as nodules composed of minute, tabular crystals. It is very soluble salt, three parts dissolving normally in just two parts of water at 18°, but it is very apt to form supersaturated soln. It is a more stable salt than the ordinary salt. Its crystals are probably anhydrous, but those analyzed showed the presence of $0{\cdot}25H_2O$ per mol.

T. Haga precipitated **tripotassium hydroxynitrilo-iso-disulphonate,** $(KSO_3)O.NK(KSO_3).2H_2O$, as an oily liquid by adding alcohol to a conc. hot aq. soln. of the disulphonate and the calculated quantity of potassium hydroxide. The oily liquid slowly forms masses of microscopic tabular crystals. The salt is very soluble in water; its soln. is not precipitated by barium chloride, and it thus differs from a soln. of the ordinary salt. It has a caustic taste; and the salt explodes when heated. T. Haga, and F. Raschig observed that **dipotassium hydroxynitrilo-iso-disulphonate,** $(KSO_3)O.NH.KSO_3$, is obtained by the hydrolysis of the aq. soln. of potassium hydroxynitrilosulphonate, as in the case of the diammonium salt just described. The hydrolysis occupies about four days. The monoclinic prismatic crystals may appear as thick prisms, thin plates, or slender needles. The salt is not dimorphous. The iso-salt is about twice as soluble in water as the ordinary salt; thus, 100 parts of water at 16·4° dissolve 6·44 parts of salt; at 17·8°, 17·18 parts; and at 20°, 8·05 parts. The soln. is neutral to litmus, methyl-orange, and phenolphthalein. F. Raschig said that the salt is stable at 100°; and an excess of hydrochloric acid hydrolyzes the alkali iso-salt into sulphuric acid and hydroxylamine: $(NaSO_3)O.NH(NaSO_3)+2H_2O=NH_2OH.H_2SO_4+Na_2SO_4$, with the possible intermediate formation of *iso-monosulphonic acid.* T. Haga prepared **trisodium hydroxynitrilo-iso-disulphonate,** $(NaSO_3)O.NNa(NaSO_3)_2.2H_2O$, by the same method as that used for the tripotassium salt. The mol. magnitudes of the anhydrous ordinary and iso-salts are related as 233, and 256·4. T. Haga prepared **disodium hydroxynitrilo-iso-disulphonate,** $(NaSO_3)O.NH(NaSO_3)$, which, like the ordinary salt, is anhydrous. Thus, a soln. of sodium hydroxynitrilotrisulphonate in five times its weight of water and acidified with dil. sulphuric acid, will be completely hydrolyzed in two or three days at the ordinary temp.; the soln. is then to be neutralized with sodium carbonate; and on exposure for a night in the ice-chamber, almost all the sodium sulphate will crystallize out, and the mother-liquor can be evaporated to obtain the required salt. Like the ordinary iso-salt, it forms hard masses firmly adhering to the sides of the vessel. These masses are stellar or warty groups of microscopic, thick, rhombic plates. The salt is exceedingly soluble in water, from which it can be nearly all precipitated by alcohol. The hydrolysis of the salt at 95° is represented by $3\{(NaSO_3)O.NH(NaSO_3)\}+3H_2O=N_2+NH_4(HSO_4)+4Na(HSO_4)+Na_2SO_4$.

T. Haga did not obtain **barium hydroxynitrilo-iso-disulphonate** in a state suited for a satisfactory determination of the nature of the salt. The evaporation of a soln. of the ammonium salt with excess of barium hydroxide in a vacuum over sulphuric acid to a small volume removed all ammonia. After removal of the excess of barium hydroxide by carbon dioxide, the filtered soln. was further evaporated in the desiccator. First a viscid and then a bulky, friable, porous mass, devoid of crystalline character, were obtained. The latter was not quantitatively analyzed, but it yielded, when hydrolyzed, barium sulphate and hydroxylamine sulphate in crystals, which were further identified by a very satisfactory acid determination. The product was therefore undoubtedly a barium iso-salt. By using less barium hydroxide, crystallized **ammonium barium hydroxynitrilo-iso-disulphonate,** $6\{(NH_4SO_3)O.NH(NH_4SO_3)\}.Ba(SO_3)_2ONH$, was formed.

W. Flügel prepared the following sparingly soluble salts: **cobalt nitritopentamminohydroxynitrilodisulphonate,** $[Co(NH_3)_5(NO_2)]HO.N(SO_3)_2$; **cobalt iso-nitritopentamminohydroxynitrilodisulphonate,** $[Co(NH_3)_5(NO_2)]HO.N(SO_3)_2$; **cobalt iso-hexamminohydroxynitrilodisulphonate,** $[Co(NH_3)_6]HO.N:(SO_3)_2$; **cobalt iso-chloropentamminohydroxynitrilodisulphonate,** $[Co(NH_3)_5Cl]HO.N:(SO_3)_2$; **cobalt-cis-isodinitrotetramminohydroxynitrilodisulphonate,** $[Co(NH_3)_4(NO_2)_2]_2HO.N:(SO_3)_2$; and **cobalt trans-iso-dinitritotetramminohydroxynitrilodisulphonate,** $[Co(NH_3)_4(NO_2)_2]_2HO.N.(SO_3)_2$.

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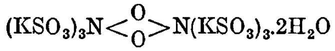
§ 58. Nitrilotrisulphonic Acid and its Salts

Among the sulphazotized salts discovered by E. Frémy,[1] there are two which result from the oxidation of one of the potassium hydroxynitrilodisulphonates in aq. soln. of either silver oxide or lead dioxide. One of these is the unstable salt, which crystallizes from the violet-blue aq. soln. in golden yellow needles, which he called *sulphazite de potasse*; and the other, which he called *metasulphazilate de potasse*, crystallizes in colourless rhombic prisms which are so well defined that he said: *Je considère ce sel comme le plus beau de tous les sels sulfazotés.* E. Frémy's analysis of the metasulphazilate was correct, $H_6O_{23}N_2S_6K_6$, which F. Raschig regards as being constituted:



$$(KSO_3)_3N<\substack{O\\O}>N(KSO_3)_3.2H_2O$$

A. Claus called this salt *trisulphoxyazoate*, and represented it by the formula $O:N(KSO_3)_3.H_2O$. In both formulæ, the nitrogen is considered to be quinquevalent. A. Hantzsch and W. Semple rejected F. Raschig's formula, and adopted that of A. Claus. F. Raschig doubled the empirical formula because the salt is not formed by the oxidation of potassium nitritotrisulphonate, but A. Hantzsch and W. Semple said that this argument has little weight when it is known that the oxidation of the tertiary ammonium derivatives does not yield amine oxides, ONR_3. The determination of the mol. wt. of the potassium sat. by cryoscopic and electrical conductivity methods is unsatisfactory. The monomolecular formula is preferred by analogy with dibenzyl nitrilotrisulphonate, $(C_6H_5SO_3)O.N(C_6H_5SO_3)_2$. T. Haga's cryoscopic observations agree with the simple formula, although the hemihydrated character of the ammonium and potassium salts suggests the doubled formula. T. Haga argued that the metasulphazilate is a triacylated hydroxylamine, $(KSO_3)_2:N.O(KSO_3)$, in which the nitrogen is tervalent. All other compounds of this type appear to have a more complex constitution—*e.g.*, W. Lossen's formula for dibenzhydroxamic acid. This view is in agreement with the scheme in which the metasulphazilates are considered to be **nitrilotrisulphonates,** $(KSO_3)(ON)(KSO_3)_2$. The free acid—**nitrilotrisulphonic acid,** $(HSO_3)(ON)(HSO_3)_2$—has not been isolated. A. Claus, and E. Frémy found that when the potassium salt is treated with hydrofluosilicic acid, the free acid is formed as potassium fluosilicate is precipitated, but the acid immediately decomposes into sulphuric acid, ammonia, and nitrogen. According to T. Haga, when the soln. of a salt is acidified, it forms hydroxynitrilo-iso-disulphonate (*q.v.*);

sulphites have no action on the salts; and sodium amalgam, or a warm copper-zinc couple, reduces the acid to imidosulphonic acid: $(HSO_3)O.N(HSO_3)_2+H_2=H_2SO_4+NH(HSO_3)_2$.

T. Haga prepared **ammonium nitrilotrisulphonate,** $(NH_4SO_3)(ON)(NH_4SO_3)_2.\frac{1}{2}H_2O$, by digesting the basic lead salt with ammonium carbonate, evaporating the soln. on a water-bath until it has almost lost its alkalinity, and concentrating it under reduced press. over solid potassium hydroxide. The thick, rhombic plates and prisms are probably isomorphous with those of the potassium salt. The salt is neutral to litmus and methyl-orange, and closely resembles the potassium salt in its properties. It is very soluble, 100 parts of water dissolving nearly 164 parts of salt. E. Frémy, A. Claus, F. Raschig, and T. Haga prepared **potassium nitrilotrisulphonate,** $(KSO_3)O.N(NH_4SO_3)_2.\frac{1}{2}H_2O$, by gently boiling the somewhat alkaline soln. of potassium hydroxynitrilodisulphonate with silver oxide or lead dioxide until the violet soln. just loses its colour. The evaporation of the filtered soln. furnishes crystals of the salt. The main reaction is: $2PbO_2+3\{HO.N(KSO_3)_2\}+KOH=2Pb(OH)_2+KNO_2+2\{(KSO_3)(ON)(KSO_3)_2\}$, along with a little sulphate, amidosulphonate, nitrogen, and nitrous oxide. Yields as high as 87·8 per cent. have been obtained. F. Raschig also obtained the salt by allowing the yellow pernitrosyldisulphonate to stand for some days in contact with water, and recrystallized the colourless residue from water. The crystals are flattened monoclinic prisms which, according to A. Fock, have the axial ratios $a:b:c=3\cdot7602:1:2\cdot0763$, and $\beta=87°\ 42'$. A. Claus said that the salt dissolves freely in water, and that the soln. can be boiled without decomposition; and F. Raschig added that it can be repeatedly crystallized from alkaline liquids without change. According to T. Haga, 100 parts of water at 18° dissolve 3·9 parts of the salt. The soln. is neutral to litmus, phenolphthalein, methyl-orange, and other indicators. When slowly heated to 100°–120° in air, it loses some water of crystallization, and is then hydrolyzed by the remainder acting together with the moisture of the atm. Hence there is first a loss of weight and then a gain. The residue is strongly acid owing to the presence of hydrosulphate. It has not been found possible to obtain the anhydrous salt because of the hydrolytic action which occurs even in a current of dry air. A. Claus found that when heated with soda-lime, one-third of the nitrogen is given off as ammonia: $3\{(KSO_3)O.N(KSO_3)_2\}+9KOH=9K_2SO_4+N_2+3H_2O+NH_3$. E. Frémy, and A. Claus found that the salt is not decomposed by nitric acid or other dil. acids; but F. Raschig, and T. Haga found that when the salt is boiled in dil. hydrochloric acid, hydroxynitrilo-monosulphonic acid is formed. F. Raschig said that an acidic soln. of permanganate is reduced by the salt, and A. Claus obtained no precipitation with soln. of the metal salts, although with lead salts a complex salt is formed which is decomposed by water. The inactivity of the sulphites towards the hydroxynitrilotrisulphonates, and the reducing action of sodium amalgam and the copper-zinc couple has been already indicated. T. Haga prepared **sodium nitrilotrisulphonate,** $(NaSO_3)(ON)(NaSO_3)_2.2H_2O$, by boiling a soln. of the disulphonate with the eq. amount of sodium hydroxide, and lead dioxide. It is more difficult than the potassium salt to purify, but by the cautious addition of sulphuric acid, the impurities can be converted into sulphates which can be removed from the soln. by freezing. It crystallizes in aggregates of small, tabular, monoclinic crystals. The solubility of the salt is considerable, 100 parts of water at 21·5° dissolve 35 parts of salt. Like the potassium salt, it is neutral to indicators, and when heated, it hydrolyzes in its water of crystallization. The mol. wt. of the salt by the cryoscopic method agrees with the simple formula. T. Haga also found that **lead hydroxynitrilotrisulphonate,** $(PbOH.PbO.SO_3)(ON)(PbOH.PbO.SO_3)_2.3H_2O$, is the only insoluble compound formed when a warm soln. of the potassium salt is poured into a soln. of basic lead acetate. The chalky white powder is readily decomposed by a soln. of an alkali carbonate. F. Ephraim and W. Flügel added different cobaltic ammines to a soln. of the potassium salt and obtained **cobaltic hexamminonitrilotrisulphonate,** $[Co(NH_3)_6]SO_3.ON:(SO_3)_2$; **cobaltic aquopentam-**

minonitrilotrisulphonate, $[Co(NH_3)_5(H_2O)]SO_3.ON:(SO_3)_2$; **cobaltic cis-dinitritotetramminonitrilotrisulphonate,** $[Co(NH_3)_4(NO_2)]\{SO_3.ON:(SO_3)_2\}_2$, as well as **cobaltic trans-dinitritotetramminonitrilotrisulphonate** ; and **cobaltic nitritopentamminonitrilotrisulphonate,** $[Co(NH_3)_5(NO_2)]SO_3.ON:(SO_3)_2$.

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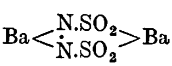
[1] E. Frémy, *Ann. Chim. Phys.*, (3), **15**. 408, 1845 ; A. Claus, *Ber.*, **4**. 508, 1871 ; *Liebig's Ann.*, **158**. 205, 1871 ; F. Raschig, *ib.*, **241**. 223, 1887 ; *Schwefel- und Stickstoffstudien*, Leipzig, 128, 1924 ; A. Hantzsch and W. Sempel, *Ber.*, **28**. 2744, 1895 ; W. Lossen, *ib.*, **25**. 440, 1892 ; T. Haga, *Journ. Chem. Soc.*, **85**. 78, 1904 ; *Journ. Coll. Science Tokyo*, **19**. 15, 1904 ; A. Fock, *Zeit. Kryst.*, **14**. 535, 1888 ; W. Flügel, *Jahrb. Phil. Fakultät Bern*, **4**. 84, 1924 ; F. Ephraim and W. Flügel, *Helvetica Chim. Acta*, **7**. 724, 1924.

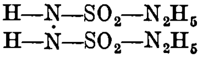
§ 59. Hydrazinosulphinic and Hydrazinosulphonic Acids

According to F. Ephraim and H. Piotrowsky,[1] when sulphur dioxide is slowly passed into a cooled soln. of hydrazine in absolute alcohol, a white crystalline precipitate of **hydrazine hydrazinodisulphinate,** $N_2H_2(HSO_2.N_2H_4)_2$, is formed. It sinters at 50°, and gives a cloudy liquid at 70°–80°, which decomposes with the evolution of gas. The aq. soln. is weakly acid, and smells slightly of sulphur dioxide; when treated with a soln. of a barium salt, it furnishes a precipitate of **barium hydrazinodisulphinate,**



$$Ba<\begin{array}{l}N.SO_2\\ N.SO_2\end{array}>Ba$$

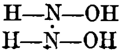
in which the hydrogen atoms of hydrazine as well as those of the sulphinic radicle are replaced by barium. The salt gradually decomposes with the loss of nitrogen. Impure **silver hydrazinodisulphinate** was similarly obtained, as well as **calcium hydrazinodisulphinate,** and **lead hydrazinodisulphinate.** The parent acid, **hydrazinodisulphinic acid,**



$$\begin{array}{l}H-N-SO_2-N_2H_5\\ H-N-SO_2-N_2H_5\end{array}$$

has not been isolated. For the action of hydrazine on sulphur, hydrogen sulphide, sulphur trioxide, and thionyl chloride, see the chemical properties of these substances. In the case of thionyl chloride, there are indications of the formation of a hydrazine of sulphurous acid.

There are derivatives of hydrazine in which one or more of the hydrogen atoms are replaced by the sulphonic radicle. R. Stollé and K. A. Hoffmann passed carbon dioxide into a well-cooled, conc. aq. soln. of hydrazine and obtained **hydrazinocarboxylic acid,** $NH_2.NH.COOH$, as a white powder which can be dried over sulphuric acid in an atm. of carbon dioxide. When heated to 90°, it decomposes into carbon dioxide and **hydrazine hydrazinocarboxylate,** $N_2H_4.NH_2.COOH$, which distils at 140° under ordinary press., forming a clear, viscous liquid which when kept over sulphuric acid forms a crystalline mass, melting at 70°. It forms an alkaline soln. with water ; and it is rapidly decomposed by acids ; when heated to 140° in a closed tube, it forms some carbohydrazide ; and when treated with ethyl chlorosulphonate, it yields **hydrazinodisulphonic acid,** $NH_2.N(HSO_3)_2$, or $HSO_3.NH.NH.HSO_3.H_2O$, which can be isolated in the form of **potassium hydrazinodisulphonate,** $N_2H_2(KSO_3)_2.H_2O$, which crystallizes from water in transparent prisms. The acid does not yield a condensation product with benzaldehyde. F. Raschig prepared the potassium salt by the action of chlorosulphonic acid on a mixture of hydrazine sulphate and pyridine ; and the potassium salt is decomposed by alkali hydroxide : $N_2H_2(KSO_3)_2+2KOH=N_2+2K_2SO_3+2H_2O$. F. Raschig suggested that dihydroxyimide, or **dihydroxyhydrazine,**



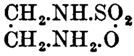
$$\begin{array}{l}H-N-OH\\ H-N-OH\end{array}$$

is formed as an intermediate product because no nitrogen and no sulphite are formed when the alkali hydrazinodisulphonate is treated with alkali-lye cooled by ice; only when the temp. rises to, say 15°, is nitrogen evolved and alkali sulphite formed.

E. Konrad and L. Pellens prepared **pyridine hydrazinodisulphonate** by the action of chlorosulphonic acid on a suspension of hydrazine sulphate in cold pyridine and subsequently precipitating the salt with ethyl alcohol. The corresponding *ammonium, sodium, and barium hydrazinodisulphonates* were prepared respectively with 1, 2, and 3 mols of water of crystallization.

W. Traube and O. Vockerodt found that when dry air is slowly drawn through a flask containing fuming sulphuric acid rich in sulphur trioxide, and then through a flask containing anhydrous hydrazine, a considerable quantity of **hydrazine hydrazinomonosulphonate,** $N_2H_2.H_2N.NH.HSO_3$, is formed, and when the aq. soln. of this product is dissolved in water, and the soln. heated with an excess of barium hydroxide, to drive off the free hydrazine, the excess of barium precipitated by carbon dioxide, and the filtrate evaporated in vacuo, **barium hydrazinomonosulphonate,** $Ba(N_2H_3.SO_3)_2.2H_2O$, is formed. When the aq. soln. is precipitated with alcohol, the salt is obtained in glistening needles. By treating the barium salt with sulphuric acid, free **hydrazinomonosulphonic acid,** $N_2H_3.HSO_3$, is formed; and the white needles of the acid melt with decomposition at 217°. By treating the barium salt with ammonium carbonate, **ammonium hydrazinomonosulphonate,** $N_2H_3(NH_4SO_3)$, is formed as a deliquescent, crystalline mass. A. P. Sabanéeff noted that this ammonium salt is isomeric with hydrazine amidosulphonate. By treating the barium salt with a suitable alkali sulphate, acicular crystals of **potassium hydrazinomonosulphonate,** $N_2H_3(KSO_3)$, and monoclinic plates of **sodium hydrazinomonosulphonate,** $N_2H_3(NaSO_3).H_2O$, were produced. The salts are stable in alkaline and neutral soln., but are decomposed by acids into sulphuric acid and hydrazine. F. Raschig said that the salt reacts with iodine in acetic acid soln.: $N_2H_3.KSO_3+2I_2+H_2O=N_2+4HI+KHSO_4$; and when treated with potassium permanganate, nitrogen gas is evolved, and two hydrogen atoms are removed, forming potassium diazomonosulphonate, $NH:N(KSO_3)$, which then breaks down into nitrogen and potassium hydrosulphite. Ammoniacal silver nitrate is rapidly reduced by these salts, but the barium salt and silver nitrate furnishes acicular crystals of **silver hydrazinomonosulphonate,** $N_2H_3.AgSO_3$. By applying the method used for the barium salt to the other alkaline earths, **calcium hydrazinomonosulphonate,** $Ca(N_2H_3.SO_3)_2.H_2O$, and **strontium hydrazinomonosulphonate,** $Sr(N_2H_3.SO_3)_2.2H_2O$, were formed.

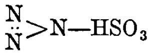
When the barium salt is treated with an aldehyde, *e.g.* salicylaldehyde or benzaldehyde, *barium hydroxybenzylidenehydrazinomonosulphonate,* $(OH.C_6H_4.CH:N.NH.SO_3)_2Ba.2H_2O$, and *barium benzylidenehydrazinomonosulphonate,* $(CH.C_6H_5:N.NH.SO_3)_2Ba.2H_2O$, were formed. If ethylenediamine be sulphonated like hydrazine, *barium ethylenediaminomonosulphonate,* $(NH_2.CH_2.CH_2.NH.SO_3)_2Ba$, is formed; and when this is treated for the free acid, there are formed colourless leaflets of *ethylenediaminomonosulphonic acid,* $NH_2.CH_2.CH_2.NH.HSO_3$. or



$$\begin{array}{l}CH_2.NH.SO_2\\ CH_2.NH_2.O\end{array}$$

E. Konrad and L. Pellens found that if pyridine hydrazinodisulphonate be oxidized by sodium hypochlorite in the presence of water at —20°, and the liquid treated with potassium chloride, **potassium diazodisulphonate,** $N_2(KSO_3)_2$, or $KSO_3.N:N.KSO_3$, is formed. The parent acid, diazodisulphonic acid, $HSO_3.N:N.HSO_3$, has not been isolated. F. Raschig said that **potassium diazomonosulphonate,** $H.N:N.KSO_3$, which he called *potassium diimidomonosulphonate,* is formed as an unstable intermediate product in the oxidation of potassium hydrazinomonosulphonate by potassium permanganate. The parent acid, **diazomonosulphonic acid,** $H.N:N.HSO_3$, has not been isolated.

W. Traube and O. Vockerodt observed that a well-cooled, conc., aq. soln. of potassium nitrite when treated with finely powdered hydrazine monosulphonate, reacts: $NH_2.NH.HSO_3+KNO_2=2H_2O+N_3.KSO_3$, and the resulting **potassium triazomonosulphonate**, $N_3.KSO_3$, is obtained in an impure state by spontaneous evaporation. When purified, it furnishes long, flat prisms which explode on heating. The parent acid, **triazomonosulphonic acid**, $N_3.HSO_3$,



$$\genfrac{}{}{0pt}{}{N}{\ddot{N}}{>}N{-}HSO_3$$

has not been isolated. They obtained, in a similar manner, **sodium triazomonosulphonate**, $N_3.NaSO_3$; **ammonium triazomonosulphonate**, $N_3.NH_4SO_3$; and **barium triazomonosulphonate**, $(N_3.SO_3)_2Ba$.

References.

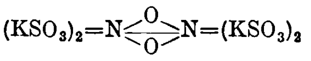
[1] R. Stollé and K. A. Hoffmann, *Ber.*, **37**. 4523, 1904; E. Konrad and L. Pellens, *ib.*, **59**. B, 135, 1926; W. Traube and O. Vockerodt, *ib.*, **47**. 938, 1914; F. Ephraim and H. Piotrowsky, *ib.*, **44**. 379, 386, 1911; H. Piotrowsky, *Ueber die Einwirkung von Ammoniak und Hydrazin auf Verbindungen des Schwefels*, Bern, 1911; F. Raschig, *Schwefel- und Stickstoffstudien*, Leipzig, 188, 1924; A. P. Sabanéeff, *Journ. Russ. Phys. Chem. Soc.*, **31**. 375, 1899; *Zeit. anorg. Chem.*, **17**. 480, 1898.

§ 60. Peroxyamidodisulphonic Acid and its Salts

The soln. of the *sulphazites* of E. Frémy[1] prepared by oxidizing a potassium hydroxynitrilodisulphonate with silver oxide or lead dioxide have an intense violet-blue colour, and furnish golden-yellow crystals. He represented the composition of the potassium salt by $HO_7NS_2K_2$, which, said A. Claus, would agree with the formula at present employed if the hydrogen be omitted. T. Haga showed that other oxidizing agents produce the violet coloration—*e.g.*, ozone, nitrous fumes, and acidified soln. of a nitrite—but hydrogen dioxide, potassium ferricyanide, potassium permanganate, alkaline cupric soln., and mercuric oxide have no perceptible action. A. Claus showed that the production of the coloured salt is not necessarily accompanied by a sulphate; that it is a product of oxidation; and that it passes spontaneously into the colourless trisulphonate, a little sulphate, and gaseous nitrous oxide. He recognized the sulphonic character of the coloured salt, and named it *oxysulphazotate* to which he assigned the formula:

$$(KSO_3)_3{\equiv}N{<}\underline{\overset{O}{\quad}}{>}NO{-}KSO_3$$

A. Claus's formula.



$$(KSO_3)_2{=}N\genfrac{}{}{0pt}{}{\lessdot O \gtrdot}{\lessdot O \gtrdot}N{=}(KSO_3)_2$$

F. Raschig's formula.

where the nitrogen is quinquevalent. F. Raschig modified this formula into that just indicated. A. Hantzsch and W. Semple regarded the coloured salt as sulphonated nitrogen peroxide, and called it *nitroxyldisulphonate*, $O.N:(KSO_3)_2$, in which the nitrogen is tervalent, and oxygen univalent. The yellow crystals are supposed to have twice the mol. magnitude of the dissolved violet form by analogy with the two forms which nitrogen peroxide itself assumes. P. Sabatier investigated the violet soln. produced by the action of reducing agents—say, sulphur dioxide—on a soln. of hydroxynitrosylsulphuric acid, $NO(HO)SO_3$, in monohydrated sulphuric acid. The similarity of the colours led him to assume that the coloration is due to the presence of the acid of E. Frémy's potassium salt, constituted $O:N(HSO_3)_2$. T. Haga raised the objections that there are striking chemical contrasts in the nature of the two soln.

(i) E. Frémy's violet salt is produced by the action of lead dioxide and is not attacked by it, whereas P. Sabatier's violet acid is at once attacked by lead dioxide; (ii) The violet acid is produced by and is indifferent towards sulphur dioxide, whereas the violet salt is at once changed by this reagent; (iii) S. Sekiguchi was unable to convert E. Frémy's violet salt into P. Sabatier's violet acid, or conversely.

The sulphonic character of the violet salt was established by the work of A. Claus, and by the fact that it can be produced by the dehydrogenation of hydroxylamine disulphonate. T. Haga defended the thesis that the nitroxy-residue in the violet salt of E. Frémy's salt of **peroxylamidodisulphonic acid,** $(HSO_3)_2N.O.O.N(HSO_3)_2$—a derivative of *peroxylamine,* $H_2N.O.O.NH_2$. It is maintained that the mode of formation of the potassium salt proves that the constitution is that of a peroxide, and therefore of a peroxamide. For example, the disodium hydroxynitrilodisulphonate loses two hydrogen atoms at ordinary temp., when oxidized by ozone, silver oxide, or lead dioxide, but not by oxygen itself: $(KSO_3)_2N.O\boxed{H+H}O.N(KSO_3)_2+O\rightleftharpoons(KSO_3)_2N.O.O.N(KSO_3)_2+H_2O$. The reversion, at ordinary temp., by a reducing agent occurs so that the peroxylamidodisulphonate forms hydroxynitrilodisulphonic acid. Again, the reaction between the peroxylamidosulphonic acid and normal alkali sulphite is most probably effected through the oxygen atoms of the peroxyl-group: $(KSO_3)_2N.O.O.N(KSO_3)_2+K_2SO_3=KO.N(KSO_3)_2+(KSO_3)ON(KSO_3)_2$. T. Haga then discusses the improbability that the nitrogen atom is more than tervalent. E. Divers favours T. Haga's view of the constitution of this salt because of the reactions with potassium sulphite resulting in the formation of hydroxylinitrilotrisulphonate and disulphonates; and with water resulting in the formation of nitrous acid and hydroxynitrilo-trisulphonate and disulphonate.

When the attempt is made to isolate **peroxylamidosulphonic acid,** $N_2O_2(KSO_3)_4$, by acidifying an aq. soln. of the potassium salt, brown fumes are evolved owing to the decomposition of the peroxylamidosulphonic acid. A. Rose possibly obtained a soln. of the acid by the action of nitric oxide on sulphuric acid: $3NO+4H_2SO_4=2H_2O+NO(HSO_3)_2+2(NO)HSO_4$. The blue liquid obtained by P. Sabatier by the action of sulphur dioxide on a soln. of hydroxynitrosylsulphonic acid in sulphuric acid may also contain this acid. As indicated below, the identity of P. Sabatier's blue acid with peroxylamidosulphonic acid has not been established. Both A. Rose's and P. Sabatier's products may be hydroxynitrosylsulphonic acid (*q.v.*).

In preparing **potassium peroxylamidosulphonate,** $N_2O_2(KSO_3)_4$, E. Frémy prepared the dipotassium or pentapotassium hydroxynitrilodisulphonates; A. Claus used the latter, F. Raschig the former. T. Haga said that the penta-salt is the better because the product is more stable in presence of the more alkaline salt, and there is consequently less loss, and the salt is more easily purified. E. Frémy preferred silver oxide as the oxidizing agent; A. Claus, lead dioxide. T. Haga found that the silver oxide gives the better yield, but lead dioxide is the more convenient oxidizing agent. The lead which contaminated the product is easily removed.

E. Frémy called this salt *sulfazilate de potasse;* A. Claus, *oxysulfazotinsäure Kalium;* and T. Haga, *potassium peroxylaminosulphonate.* T. Haga said that the unstable salt should be prepared just when it is wanted, and recommended the following process:

Mix 5 grms. of pentapotassium hydroxynitrilodisulphonate—or the dipotassium salt with a little potassium hydroxide—and a little more than the same weight of lead dioxide or silver oxide, and make up with water to 25 c.c. Agitate the mixture for 15 minutes at a temp. near to but not exceeding 40°. Decant the soln. at once, remove any lead by a current of carbon dioxide, and filter the warm soln. before crystallization sets in. Allow the mixture to stand in an ice-box for some hours when the whole of the desired salt will have separated as a crust of minute yellow needles. These can be recrystallized with a slight loss from hot water made alkaline with potassium hydroxide. If any salt has escaped oxidation, it will contaminate the yellow crystals, colouring them violet, owing, as A. Hantzsch and W. Semple observed, to hydroxynitrilodisulphonate retaining 1 to 4 per cent. of the violet soln. in solid soln.

There are some discrepant observations by E. Frémy, A. Claus, F. Raschig, and T. Haga on the properties of the potassium salt. The following are mainly from T. Haga's revision in his memoir: *Peroxylamine Sulphonates and Hydroxylamine Trisulphonates.* Solid potassium peroxylamidosulphonate is too unstable when dry and free from alkali to exist many minutes without rapidly and almost explosively decomposing. In this decomposition, slight white fumes of ammonium salt (probably pyrosulphite and pyrosulphate), nitrogen and nitrous oxide, and a small quantity of sulphur dioxide are given off, whilst the residue, when the mass of the salt has been at all considerable, becomes very hot (above 300°) and melts. This residue consists of potassium sulphate (principally pyrosulphate) with a very little ammonium salt. Sometimes a trace of amido-monosulphonate can be detected by the mercuric nitrate test; also a trace of hydroxylamine (or other substance reducing alkaline cupric soln.), but none of the other sulphonates, the temp. having been too high to leave these substances undecomposed. The true products of the spontaneous decomposition of a peroxylamidosulphonate are only found (in company with small quantities of apparently secondary products) when the salt is heated to boiling with enough water to dissolve it, and in presence of sufficient alkali to prevent both the acidification of the soln. during the decomposition of the salt and also the secondary changes which would result from acidification. The alkali does not appear to modify the nature of the primary change, although it distinctly increases the stability of the salt, as already mentioned. When carried out in the foregoing manner, the decomposition of a peroxylaminosulphonate proceeds largely in such a way that not only do three-fourths of the sulphur of the salt, as suggested by A. Claus, and by F. Raschig, together with one-half of its nitrogen, come out as hydroxylnitrilotrisulphonate, but the rest of the sulphur and one-fourth of the nitrogen become hydroxynitrilodisulphonate again, whilst the remaining one-fourth of the nitrogen appears as nitrite,

$$2(SO_3K)_4N_2O_2+H_2O=2(SO_3K)_3NO+(SO_3K)_2NOH+NO_2H,$$

although some nitrous oxide and sulphate, besides minute and uncertain quantities of other substances, are always produced. This result explains the production of the large quantities of acid sulphate and nitrous oxide observed by A. Claus, and F. Raschig, for the nitrous acid when not neutralized by alkali interacts with the hydroxynitrilodisulphonate and yields acid sulphate and nitrous oxide. The regeneration of hydroxynitrilodisulphonate in the spontaneous decomposition of a peroxylamidosulphonate accounts for the fact, met with in the present investigation, that much more hydroxynitrilotrisulphonate is obtainable by heating hydroxynitrilodisulphonate in soln. with excess of lead peroxide than can be derived from the decomposition (out of contact with lead peroxide) of the peroxylamidesulphonate equivalent to that quantity of hydroxynitrilodisulphonate.

E. Frémy was mistaken in saying that when the salt is left in a closed bottle it furnishes nitric oxide. According to T. Haga, the general character of the decomposition of the salt is as follows: the mol of peroxylamidosulphonate is halved by the hydrolysis, and converted into hydroxynitrilodisulphonate, and probably an unstable **potassium hydroxyperoxylamidosulphonate,** $HO.O.N(KSO_3)_2$, which has not been isolated: $(KSO_3)_2N.O.O.N(KSO_3)_2=HO.O.N(KSO_3)_2+HO.N(KSO_3)_2$. The unstable hydroxyperoxylamidosulphonate reacts with the original salt $N_2O_2(KSO_3)_4+HO.O.N(KSO_3)_2=HO.NO+2\{(KSO_3)O.N(KSO_3)_2\}$; and, neglecting intermediate products, this gives as a resultant equation (i): $2N_2O_2(KSO_3)_4+H_2O=HNO_2+2ON(KSO_3)_3+HO.N(KSO_3)_2$. The hydroxynitrilodisulphonate may also react with the original salt: $2N_2O_2(KSO_3)_4+2HON(KSO_3)_2=4\{(KSO_3)O.N(KSO_3)_2\}+H_2N_2O_2$, which gives the resultant equation (ii): $6N_2O_2(KSO_3)_4+H_2O=N_2O+2HNO_2+8\{(KSO_3)O.N(KSO_3)_2\}$. The sulphate found among the products of the decomposition in varying amounts does not come from the hydrolysis of the salt itself or from the reaction products hydroxynitrilotrisulphonate and disulphonate. The trisulphonate is stable in the presence of alkali, and the disulphonate yields sulphite not sulphate. T. Haga assumed that it came from the decomposition of the unstable hydroxyperoxylamidosulphonate, where it fails to react with the peroxylamidosulphonate. It may hydrolyze either according to $2\{HO.O.N(KSO_3)_2\}+H_2O=HO.N(KSO_3)_2+HNO_2+2KHSO_4$, or according to $2\{HO.O.N(KSO_3)_2\}+H_2O=N_2O+4KHSO_4$, which may be combined with the primary equation. The nitrogen which is formed may be produced in the reaction: $N_2O_2(KSO_3)_4+2H_2O=N_2+4KHSO_4$, and the potassium amidosulphonate by: $N_2O_2(KSO_3)_4+3H_2O=3KHSO_4+HNO_2+NH_2.KSO_3$. Part of the instability of the peroxylamidosulphonates is to be attributed to the presence of oxidizable impurities. Thus, E. Frémy noticed the decomposing action of atm. dust; while nitrites, liable to be present as an impurity, greatly increase its instability, and acids hasten while alkalies retard the decomposition of the salt. Potassium peroxylamidosulphonate is very unstable in water and very slightly soluble in the cold. In $\frac{1}{10}N$-KOH, which fairly represents its usual mother-liquor, it is more stable, but still not very soluble; 100 parts at 3° dissolve only 0·62 part of the salt, and, at 29°, only 6·6 parts. It interacts in soln. with normal potassium sulphite and then produces hydroxynitrilotrisulphonate and hydroxynitrilodisulphonate, evidently in mol. proportions, this change being a fact of great theoretical importance. Its chemical activity is manifested in oxidizing certain easily oxidizable substances, and being thereby reduced to its parent salt, hydroxynitrilodisulphonate. Although it liberates iodine from hydriodic acid, it fails to oxidize hydrochloric acid. When the latter acid in conc. soln. is poured on the solid salt, it sets up the same decomposition as that which occurs spontaneously. But here, as the rise of temp. is moderated, definite although minute quantities of amidomonosulphonate and of hydroxylamine (not its sulphonate) can be found. The salt has practically no action on alcohol; nitrous and sulphurous acids rapidy reduce it, so also does sodium amalgam, first to hydroxynitrilodisulphonate, as observed by P. Schatzmann, and then this salt passes slowly but completely into imidodisulphonate. Clean granulated zinc slowly reduces the salt, but copper does not. The spontaneous decomposition of the salt may, however, easily be mistaken for its slow reduction by a reducing agent, since in this case also hydroxynitrilodisulphonate is produced. The difference is readily detected by testing for nitrite, which is produced only in the spontaneous decomposition of the salt. Manganese dioxide very slowly decomposes it, causing a minute effervescence; lead peroxide is inactive. Potassium permanganate is reduced to green manganate. Clean filter-paper, unlike the paper in use in E. Frémy's time, does not affect it.

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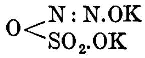
§ 61. Hyponitritosulphuric Acid and its Salts

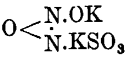
In 1835, J. Pelouze,[1] in his *Mémoire sur quelques combinaisons d'un nouvel acide formé d'azote, de soufre, et d'oxigène*, described what he called *l'acide nitrosulfurique*, or *les sels nitrosulfates*, by bringing nitric oxide in contact with alkali sulphites, or a mixture of nitric oxide and sulphur dioxide in contact with an alkali at ordinary temp. An excess of alkali promotes the formation of the compound. He added that the alkali absorbs two vols. of nitric oxide for every vol. of sulphur dioxide. If the nitric oxide predominates the excess remains unabsorbed, while if the sulphur dioxide predominates, an alkali sulphite is formed as well as the nitrosulphate. E. Divers and T. Haga emphasized the fact that these salts are formed from sulphites by a process analogous to that by which sulphates and thiosulphates are formed from sulphites, namely, by leaving a soln. of a normal sulphite in contact with nitric oxide, oxygen, or sulphur as the case requires. The nitrosulphates of

J. Pelouze also revert to nitric oxide and sulphite. Hence, as in the case of, say, calcium thiosulphate, $CaS_2O_3 \rightleftharpoons CaSO_3+S$, so in the case of the nitrosulphates, $K(N_2O_2).SO_2.OK \rightleftharpoons K.SO_2OK+N_2O_2$; and in the case of sulphates, $KO.SO_2.OK \rightleftharpoons K.SO_2.OK+O$. Again, sodium amalgam acts on a thiosulphate, forming sulphite and sulphur, so on a nitrosulphate it forms sulphite and hyponitrite. The sulphonate constitution was advocated by F. Raschig, W. Traube, A. Hantzsch, and P. Duden, but other formulæ have been suggested:



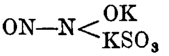
$$O<\genfrac{}{}{0pt}{}{N:N.OK}{SO_2.OK}$$

E. Divers' formula.



$$O<\genfrac{}{}{0pt}{}{\dot{N}.OK}{\dot{N}.KSO_3}$$

A. Hantzsch's formula.



$$ON-N<\genfrac{}{}{0pt}{}{OK}{KSO_3}$$

F. Raschig's formula.

F. Raschig said that the potassium salt is best obtained by the action of nitric oxide on a 40 per cent. soln. of potassium sulphite as indicated below. E. Divers showed that the ordinary nitrogen-sulphonic compounds give a precipitate of barium sulphate with an acidified soln. of barium chloride only after standing an appreciable time, while the nitrosulphates give a precipitate immediately. Again, alone in aq. soln. the potassium salt slowly decomposes into normal sulphate and nitrous oxide, whereas in the presence of a little alcohol, potassium ethyl sulphate, potassium hydroxide, and nitric oxide are formed: $KO.SO_2.O.N:NOK+C_2H_5OH=(C_2H_5)KSO_4+KOH+N_2O$; it is extremely probable that the nitrous oxide is formed by the decomposition of the potassium hydrohyponitrite, $KO.N_2.OH$, of W. Zorn, so that the reaction is formulated: $KON_2.KSO_4+C_2H_5OH=(C_2H_5)KSO_4+KO.N_2OH$. F. Raschig's formula is well suited to explain the decomposition of the salt into sulphate and nitrous oxide, but it does not account very well for the action of sodium amalgam in harmony with that of other sulphonates; similarly, P. Duden's explanation of the action of potassium hydroxide by means of F. Raschig's formula does not make it clear why a sulphate is formed when other sulphonates under similar conditions yield sulphites. P. Duden's synthesis of hydrazine by the reduction of the nitrosulphate does not agree with the sulphonic character of these salts. A. Lachman and J. Thiele also showed that while all undoubted sulphonates give nitrous oxide, and sometimes a little nitramide, when mixed in the cold with nitric and sulphuric acids, potassium nitrosulphate does not do so. E. Divers and T. Haga also found that while the amidosulphonates, oxygenated or not, resist the action of sodium amalgam, the nitrosulphates are at once reduced, showing that the latter are probably not sulphonates. In conclusion, it is urged that the hyponitrite-sulphate formula explains every known chemical action of these salts while the sulphonic formula explains only some of them and suggests others they do not possess. The dibasic acid is therefore named **hyponitritosulphuric acid,** $HO.N:N.HSO_4$, and the salts **hyponitritosulphates.**

J. Pelouze prepared crystals of **ammonium hyponitritosulphate,** $(NH_4)_2SO_3N_2O_2$, by allowing a soln. of ammonium sulphite, cooled by a freezing mixture, to absorb nitric oxide. At 0° and upwards, the soln. decomposes into nitrous oxide and ammonium sulphite, but the reaction is retarded if the soln. be mixed with three times its vol. of aq. ammonia. The crystals were washed with aq. ammonia and dried between bibulous paper. The clear, rhombic prismatic crystals have a slightly bitter taste, and a neutral reaction. The crystals can be heated to 110°, but above that temp., they decompose with an explosion, forming nitrous oxide. They decompose with sparking when thrown on red-hot coals. They can be dissolved in water, but the salt in aq. soln. soon decomposes: $N_2O_2.(NH_4)_2SO_3=N_2O+(NH_4)_2SO_4$. The decomposition at 0° is slow, but very rapid at 40°; the speed of the reaction is accelerated by the presence of carbon, pyrolusite, silver oxide, and platinum sponge. The salt does not reduce manganic sulphate or indigo soln.; it is decomposed by acids and metal salts. It is insoluble in hot alcohol, and is precipitated by alcohol from its aq. soln. J. Pelouze prepared **potassium hyponitritosulphate,** $K_2SO_3.N_2O_2$, as indicated above. The salt was also prepared by A. Claus. F. Raschig reported another modification. He said that one isomer gives a precipitate with barium chloride which is insoluble in water, but which dissolves in hydrochloric acid to form a soln. which remains clear for a short time and then deposits barium sulphate; the other isomer, obtained only once, gives no precipitate with barium chloride, though on adding hydrochloric acid, barium sulphate is immediately precipitated. This was not confirmed by A. Hantzsch, E. Divers and T. Haga, and C. M. Luxmore.

A. Hantzsch prepared the salt by dissolving one-fourth of a weighed quantity of potassium hydroxide in a little water, and sat. the soln. with sulphur dioxide so as to form hydrosulphite; the remainder of the potassium hydroxido was added, and mixod with the necessary amount of water for its dissolution. The air was displaced by a fast current of nitric oxide, and the liquid sat. with the gas. The alkaline liquor was thon decanted from the crystals, which were washed twice with iced-water. E. Divers and T. Haga displaced the air by a stream of hydrogen; and recommended using vessels which exposed a large surface of liquid to the nitric oxide gas. They used a soln. containing 40 per cent. of potassium sulphite, and 5 per cent. of potassium hydroxide. The crystals wcro purified, if necessary, by dissolving them quickly, at 50°–60°, in 4 to 5 times their weight of water containing 1 to 1½ per cent. of potassium hydroxide. The recrystallization involves considerable loss.

F. Raschig said that that salt is not attacked by potassium permanganate in acidic soln.; but it is oxidized by sodium hypochlorite in the presence of a little water. The usual products of decomposition are nitrous oxide and potassium sulphate; nitric oxide and potassium sulphite can be obtained from it by boiling with potassium hydroxide soln., or by fusion; and hydrazinosulphonic acid, by alkaline reduction. He said that the formation of the hyponitritosulphate can be explained by assuming, with A. Hantzsch, that before the combination, nitric oxide forms double mols, and also that both potassium atoms in potassium sulphite are joined to the sulphur atom. When nitric oxide reacts with potassium hydrosulphite, the first product probably has the constitution $NO.N(OK)SO_3K$, which then undergoes rearrangement. When nitric oxide is passed into a soln. of potassium hydrosulphite, potassium nitrilosulphonate, $N(SO_3K)_3,2H_2O$, is formed, which decomposes on boiling, yielding potassium hydrogen sulphate and potassium amidosulphonate. The reaction between nitric oxide and potassium hydrosulphite may be explained by assuming the formation of potassium nitroxylsulphonate, $OH.N.SO_3K$, which combines further with nitric oxide, yielding potassium nitrosohydroxylaminosulphonate, $ON.N(OH)SO_3K$, from which the potassium nitrososulphite, $ON.N(OK)SO_3K$, is formed in alkaline soln. In the absence of alkali, potassium nitrosoamidodisulphonate is obtained. In the decomposition of potassium nitroxysulphonate, $OH.N.SO_3K$, hyponitrous acid and the residue, SO_3K, are first produced. From the latter by simple association potassium dithionate results.

A. Hantzsch said that the colourless needle-like crystals are stable in dry air, but in moist air they slowly form potassium sulphate. J. Pelouze said that the crystals are irregular, six-sided columns which resemble potassium nitrate. The crystals have no smell, a slightly bitter taste, and a neutral reaction. E. Divers and T. Haga found that the drier the atm. the more slowly does the salt lose weight when heated. C. M. Luxmore observed a loss of 2·5 per cent. in five minutes a little below 105°; J. Pelouze said the salt did not lose weight at 115°. The different results are due to differences in the humidity of air and salt. J. Pelouze added that the salt decomposes at 130° into nitric oxide and potassium sulphite. A. Hantzsch, however, said that the decomposition is quantitative at 90°, and nitrous oxide is the gaseous product. E. Divers and T. Haga said that if the gas observed by J. Pelouze was nitric oxide, it must have arisen from some impurities. They added that the crystals exploded in a current of air at 91°, in an oil-bath, and at 108° in an air-bath. C. M. Luxmore found that with a thermometer immersed in the salt, explosive decomposition occurs at 127°–148°. The difference in these results is due to the spontaneous heating of the salt to about 130° before it explodes. E. Divers and T. Haga reported that 100 parts of water at 14·5° dissolve 12·5 parts of salt.

J. Pelouze showed that the salt is insoluble in alcohol, but easily soluble in water, and that the aq. soln. is fairly stable; as indicated above, E. Divers and T. Haga found the salt is decomposed by absolute alcohol, and by water. With warm water, A. Hantzsch said that the soln. gives off nitrous oxide, and effervesces, but no nitric oxide is formed. The soln. in dil. alkali-lye was found by F. Raschig to yield crystals of hydroxynitrilodisulphonate. E. Divers and T. Haga said that alkaline soln. are reduced by sodium amalgam: $KO.N_2.KSO_4+H_2=H_2SO_3+K_2N_2O_2$, forming at the same time some ammonia, nitrogen, nitrous oxide, sulphate, sulphite, amidosulphonate, but no hydroxylamine; and P. Duden found that in the cold, reduction by sodium amalgam, or by zinc-dust and ammonia or soda-lye, furnishes some hydrazine. J. Pelouze said that even the feeblest of acids decomposes potassium hyponitritosulphate; and contact with barium chloride, copper oxide, silver oxide, zinc oxide, manganese sulphate, lead acetate, and platinum-sponge decomposes the salt. As indicated above, barium chloride acts only slowly on the aq. soln., precipitating barium sulphate. A. Hantzsch said that the salt forms complex salts with the salts of the heavy metals—thus, **potassium silver hyponitritosulphate** is formed as a white mass, which decomposes at 25° with the evolution of red fumes, when soln. of the salt are treated with silver nitrate; and **potassium barium hyponitritosulphate,** when treated with barium chloride; the complex barium salt is soluble in a large proportion of water.

J. Pelouze obtained a soln. of **sodium hyponitritosulphate,** $NaO.N_2.NaSO_4$, and found it to possess properties like those of the potassium salt, and to be so soluble in water that he did not isolate it. E. Divers and T. Haga prepared the salt by exposing to an atm. of nitric oxide at ordinary temp., a conc. soln. of normal sodium sulphite mixed with $\frac{1}{40}$th of its weight of sodium hydroxide as a preservative. At the end of five days, the soln. was effervescing, and nearly all the sulphate was crystallized out by keeping the soln. for some time at a temp. a little below zero. The clear soln. was quickly evaporated in vacuo, when it deposited minute crystals. These were drained and dried on a porous tile. The crystalline powder was anhydrous, but contained about 1·4 per cent. absorbed water. The crystals tasted like common salt; they were slightly alkaline to litmus, and were free from sulphate and sulphite. Sodium hyponitritosulphate is, therefore, an anhydrous salt, like the potassium salt. Like the potassium salt also, although it continuously decomposes into sulphate and nitrous oxide when in neutral soln., it can be heated moderately with very little change, if some sodium hydroxide is present; when, however, such an alkaline and somewhat conc. soln. is boiled, it rapidly decomposes into sulphite and nitric oxide, and this the potassium salt does not do. It thus seems that the reversion of hyponitritosulphates into nitric oxide and sulphite is dependent on temp. alone, and is not prevented by the presence of water. It is otherwise with their decomposition into nitrous oxide and sulphate, which is caused either by water alone, or by elevation of temp. alone; for at the common temp. they can be kept for an apparently indefinite time when dry, but decompose in damp air or in soln.; on the other hand, when heated, even in dry air, they generally decompose much more in this way than into nitric oxide and sulphate. One exception to this is the potassium silver salt, which, when heated, gives only nitric oxide and sulphite (A. Hantzsch). This fact points to the latter decomposition as the primary effect of heat in all cases, and to the production of sulphate and nitrous oxide as the result of the interaction of nitric oxide and sulphite. Potassium silver sulphite not being readily oxidizable, this interaction does not occur when potassium silver hyponitritosulphate decomposes.

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3264, 3498, 1894; A. Claus, *ib.*, **4.** 509, 1871; W. Traube, *ib.*, **26.** 607, 1894; F. Raschig, *Schwefel- und Stickstoffstudien*, Leipzig, 108, 1924; *Liebig's Ann.*, **241.** 231, 1887; A. Lachman and J. Thiele, *ib.*, **288.** 267, 1895; W. Zorn, *Die Untersalpetrigesäure und deren organischen Derivate*, Heidelberg, 1879; *Ber.*, **11.** 1630, 1878; **12.** 1509, 1879; **15.** 1007, 1258, 1882.

§ 62. Nitratosulphuric Acid and its Salts

According to C. F. Schönbein,[1] a mixture of nitric and sulphuric acids acts as a more vigorous oxidizing agent than nitric acid alone, and produces different products. If only a small proportion of nitric acid is present, and in the cold, sulphur dioxide with very little nitrogen peroxide is evolved; if more nitric acid is present, nitric oxide is given off—*vide* the action of sulphuric acid on sulphur. The soln. dissolves selenium, and phosphorus at 0° without evolution of gas, forming selenium dioxide in the one case, and phosphorous and phosphoric acids in the other; and iodine is converted into iodic acid. A. Cahours found a mixture of hydrated sulphuric acid and fuming nitric acid converts many organic substances into nitro-compounds; and M. Dietzenbacher, that it oxidizes sulphur, and arsenic in the cold; and it inflames phosphorus, and carbon. A. Rose showed that by distilling the mixed acids some nitroxylsulphonic acid is formed. Free **nitratosulphuric acid,** $HNO_3.H_2SO_4$, or $(HO)_2NO.O.HSO_3$, has not been isolated. J. Kendall, and A. V. Saposhnikoff said that conc. nitric does not form with sulphuric acid the compound supposed to exist by W. B. Markownikoff, but the mixed soln. may contain a little free nitrogen pentoxide. W. C. Holmes reported that there is a maximum on the f.p. curves of mixtures of sulphuric and nitric acid corresponding with *nitratopentasulphuric acid,* $HNO_3.5H_2SO_4$, but C. D. Carpenter and A. Lehrman showed that the compound is really a complex **dinitratosulphato-octosulphuric acid,** $2HNO_3.8H_2SO_4.SO_3$, or $10SO_3.N_2O_5.9H_2O$; and it belongs rather to the ternary system: SO_3–N_2O_5–H_2O, although it is responsible for a maximum on the f.p. curve of the binary system—Fig. 102. The solid phases in the ternary system are illustrated by Fig. 103.

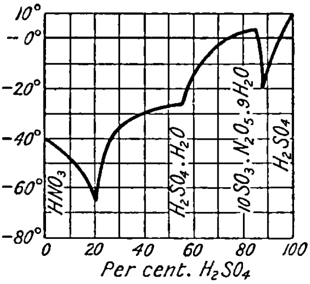

FIG. 102.—Freezing Points of the Binary System: HNO_3–H_2SO_4.

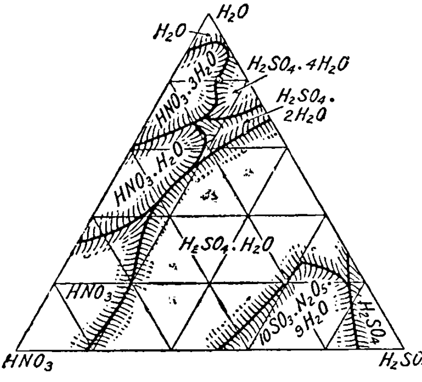

FIG. 103.—Solid Phases in the Ternary System: H_2SO_4–HNO_3–H_2O.

In the **sodium nitratosulphates** discussed in a previous volume—**2.** 20, 26, and 36—and in the potassium and ammonium nitratosulphates indicated below, C. Friedheim and J. Mozkin hold that ordinary double salts are not involved, but rather mols. with definite and atomic structures. Thus, with the potassium salt, $KNO_3.KHSO_4$, or $HNO_3.K_2SO_4$, it is argued that since no free nitric acid is given off at 140°, and water is evolved at 180°, a pyrosalt must be involved, and they express the change: $2\{KSO_3.O.NO:(OK)OH\} = KSO_3.O.NO:(OK).O(KO):ON.O.KSO_3+H_2O$. The action of a mol of sulphuric acid on two mols of ammonium nitrate in dil. soln.. followed by slow evaporation, furnished C. Friedheim and J. Mozkin with deliquescent crystals of **ammonium nitratosulphate,** $NH_4.NO_3.(NH_4)HSO_4$, or $HNO_3.(NH_4)_2SO_4$; the constitution resembles that of the potassium salt, $HO.NO(ONH_4).O.SO_2.ONH_4$. V. A. Jacquelain obtained a crop of crystals of **potassium nitratosulphate,** $KHSO_4.KNO_3$, or $K_2SO_4.HNO_3$, from a soln. of potassium sulphate in warm sulphuric acid after some crystals of potassium nitrate and hydrosulphate had separated out. The sp. gr. is 2·381, and the m.p. 150°. C. Friedheim and J. Mozkin also obtained the same salt from a soln. containing one mol of sulphuric acid and two mols of nitric acid. As indicated above, they represent the constitution $HO.NO(OK).O.SO_2.OK$.

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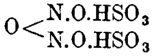
§ 63. Nitrosylsulphonic Acid, and Hydroxynitrosylsulphonic Acid

F. Raschig[1] considered that **nitrosylsulphonic acid,** $O:N.SO_2.OH$, is formed as a transient intermediate compound in the lead-chamber process for the oxidation of sulphur dioxide by nitrous acid: $HNO_2+SO_2=NO.HSO_3$ but this reacting with more nitrous acid forms hydroxynitrosylsulphonic acid: $NO.HSO_3+HNO_2=NO+ON(OH)HSO_3$. The hypothesis was discussed by G. Lunge and E. Berl, W. Manchot, F. Raschig, and O. Wentzky. F. Raschig said that nitrosylsulphonic acid decomposes in accord with the scheme: $NO.HSO_3+H_2O=NOH+H_2SO_4$, and the hyponitrous acid breaks down into nitrous oxide and water. W. C. Reynolds and W. H. Taylor said that the alleged nitrosylsulphonic acid does not exist; dil. soln. of nitrous and sulphurous acids mutually decompose one another, giving off nitrous oxide. E. Divers said that the reaction probably proceeds in two stages: $HNO_2+2H_2SO_3=HO.N(HSO_3)_2+H_2O$, and the hydroxynitrilodisulphonic acid then decomposes $HO.N(HSO_3)_2+HNO_2=2H_2SO_4+N_2O$. If, at 0°, a dil. soln. of nitrous acid is added to two mol. proportions of sulphurous acid, no gas is evolved and the intermediate hydroxynitrilodisulphonic acid is formed—if the soln. is neutralized and concentrated, the acid can be isolated—the addition of another mol. proportion of nitrous acid furnishes nitrous oxide and sulphuric acid.

W. Manchot argued that since the absorption spectrum of the blue acid does not resemble the absorption spectra of the ferrous and cupric nitrosyl salts, it is not constituted as F. Raschig supposed. F. Raschig replied:

> A soln. of sodium nitrate in conc. sulphuric acid in the absence of air acquires under the action of mercury, copper, or silver an intense blue colour, which gradually fades; the colourless soln. contains nitrous oxide. Nitrosulphonic acid forms with a soln. of sulphur dioxide in sulphuric acid a blue soln. from which nitric oxide is quantitatively evolved, $2NO_2.SO_3H+SO_2+2H_2O=2NO+3H_2SO_4$. Nitric oxide is absorbed by copper sulphate dissolved in conc. sulphuric acid in the mol. ratio 1 : 1 at atm. temp. and press.; the conception that the dark blue soln. contains the copper salt of nitrosisulphonic acid is strengthened by the observation that hydroxylaminesulphonic acid is oxidized by monopersulphuric acid in presence of sulphuric acid and a trace of copper to a dark blue compound, whereas hydroxylamine is not similarly affected.

The *blue acid* obtained by the reduction of nitroxylsulphonic acid was assumed by P. Sabatier to be a variety of peroxylamidosulphonic acid, but T. Haga, and F. Raschig did not accept this hypothesis. F. Raschig called this acid *Nitrosisulfonsäure*, and G. Lunge and E. Berl, *Sulfonitronsäure.* M. Trautz showed that it may be regarded as an intermediate stage in the reduction of nitroxylsulphonic acid. F. Raschig showed that it is produced by reducing nitroxylsulphonic acid, $O_2N.SO_2.OH$, and consequently that it is hydroxynitrosylsulphonic acid, $ON(OH)HSO_3$, *i.e.* $O{=}N(OH).SO_2.OH$, where the nitrogen has the same valency as in nitrogen peroxide. O. Wentzky represented the acid by the constitutional formula:



$$O<\begin{matrix}N.O.HSO_3\\N.O.HSO_3\end{matrix}$$

and called it *nitrosylous sulphuric acid.* He assumed that P. Sabatier's blue acid is formed by the reaction: $2NO_2.HSO_3+H_2SO_3=H_2SO_4+O(NO.HSO_3)_2$, by the removal of an atom of oxygen from two mols of nitroxylsulphonic acid, and not, as F. Raschig supposed, by adding an atom of hydrogen to a mol of nitroxylsulphonic acid. Both E. Divers, and O. Wentzky showed that only sulphur dioxide is evolved by the action of mercury on sulphuric acid, and that magnesium, which does furnish hydrogen, does not produce the blue acid when it acts on a soln. of nitroxylsulphonic acid in sulphuric acid. As shown by W. C. Reynolds and W. H. Taylor, P. Sabatier's blue acid can be formed only in soln. containing the nitroxylsulphonic acid. The acid has not been isolated, but G. Lunge and E. Berl synthesized it in conc. sulphuric acid soln. by mixing liquid sulphur dioxide, and liquid nitrogen peroxide and water at —15°, $NO_2+SO_2+H_2O=NO(HO)HSO_3$. F. Raschig said that hydroxynitrosylsulphonic acid is stable in sulphuric acid soln. It is also formed by reducing nitrosylsulphonic acid with copper or mercury in sulphonic acid soln. The soln. is very unstable, for it quickly decomposes into nitric oxide and sulphuric acid. Hydroxynitrosylsulphonic acid forms a blue soln. with conc. sulphuric acid; with more dil. sulphuric acid, it forms a red coloration, which becomes violet when copper sulphate is added; it is very unstable, the products of its decomposition being nitric oxide and sulphuric acid. With copper and iron respectively, it forms compounds of the nature of salts, the soln. of which in conc. sulphuric acid do not give off nitric oxide on being agitated. According to F. Raschig, nitric oxide is evolved when nitrous and sulphurous acids react in the presence of a great excess of sulphuric acid; and if sulphuric acid be absent, nitrous oxide is evolved. In both cases, potassium iodide was added to show if an excess of nitrous acid was present. W. C. Reynolds and W. H. Taylor said that instead of assuming the formation of F. Raschig's nitrosisulphonic acid, the phenomena are better explained from the fact that nitrous acid and potassium iodide in the presence of a mineral acid react: $2HNO_2+2HI=2NO+I_2+2H_2O$; and if sulphurous acid be also present, it is oxidized by the iodine: $H_2SO_3+H_2O+I_2=H_2SO_4+2HI$, and the cycle is repeated. A trace of potassium iodide thus acts as a catalyst converting sulphurous into sulphuric acid at the expense of the nitrous acid. The reactions indicated above by E. Divers proceed simultaneously with these changes; and thus the gaseous product is a mixture of nitrous and nitric oxides.

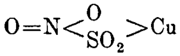
In F. Raschig's theory of the lead-chamber process, nitrosylsulphonic acid is supposed to react with nitrous acid, forming this acid: $NO.SO_2.OH+HNO_2=NO+NO(OH)HSO_3$. He also made the blue acid by dissolving 10 grms. of powdered sodium nitrite in 100 c.c. of conc. sulphuric acid, and after shaking to dissolve as much of the nitrite as possible, adding 10 grms. of sodium hydrosulphite, when the yellow soln. becomes blue. If the blue colour does not soon appear, add 10 c.c. of cold water. The blue acid soln. was also made by passing nitric oxide into a mixture of 10 c.c. of a sat. soln. of copper sulphate and 200 c.c. of conc. sulphuric acid. The reaction does not occur in the absence of the cupric sulphate, although ferrous sulphate does quite well. The blue acid soln. was obtained by F. Raschig by the oxidation of a soln. of 1·35 grms. of sodium hydroxynitrilomonosulphonate in 2 c.c. of water by mixing it with 10 c.c. of N-$CuSO_4$ and 100 c.c. of conc. sulphuric acid. The blue colour soon vanishes because the oxidation continues until nitroxylsulphonic acid is formed. E. Scandola said that the blue acid is best obtained by mixing conc. sulphuric acid with a few drops of nitric acid and some drops of alcohol; and then with a cold conc. soln. of copper sulphate, and heating. A. Guremann obtained the violet soln. about the cathode during the electrolytic reduction of a soln. of 0·00316 grm. nitrogen trioxide per c.c. of sulphuric acid of sp. gr. 1·837 using a current 0·1 amp. and 4 volts. The possible part played by hydroxynitrosylsulphonic acid in the lead-chamber process for sulphuric acid has been discussed by G. Lunge and E. Berl, and S. Littmann. J. W. Döbereiner observed a violet-blue coloration is produced during the reduction of nitroxylsulphonic acid by the metals, and F. Raschig said that a soln. of nitrosylsulphonic acid in sulphuric acid, or sodium nitrite in a great excess of conc. sulphuric acid is coloured violet-blue, and a little nitric oxide is evolved, when treated with numerous organic and inorganic reducing agents—*e.g.* sulphurous acid, hypophosphorous acid, mercury, etc.

Cuprous oxide, chloride, bromide, iodide, or thiosulphate, or cuprosic salts, or reduced copper effect the reduction in a decisive manner. The reaction is very slow with copper foil. F. Raschig agitated a soln. of 69 grms. of sodium nitrite in a litre of conc. sulphuric acid, with much copper-foil for 15 minutes, and obtained the violet-blue acid; he also added nitroxylsulphonic acid to a mixture of 10 c.c. of a sat. soln. of copper sulphate with 200 c.c. of conc. sulphuric acid, and agitated the mixture after the addition of mercury. This soln. of hydroxynitrosylsulphonic acid is fairly stable; it is oxidized by potassium permanganate to nitroxylsulphonic acid without the evolution of gas; it is likewise oxidized by a $\frac{1}{10}N$-soln. of nitric acid in conc. sulphuric acid. G. Lunge and E. Berl said that hydroxynitrosylsulphonic acid is not oxidized by oxygen alone, but it is instantly oxidized by nitrogen peroxide at −15°. F. Raschig found that the blue coloration is produced in a soln. of nitroxylsulphonic acid in sulphuric acid by silver, cadmium, mercury, aluminium, tin, lead, and antimony. The blue produced with cobalt is very unstable, while zinc, phosphorus, bismuth, sulphur, chromium, and uranium produce no blue coloration. Magnesium, thallium, arsenic, and reduced nickel are very active chemically, but give no blue coloration. Selenium and tellurium react as with sulphonic acid alone. No positive results were obtained with arsenic and antimony trioxides; mercurous and chromous chlorides; manganous and stannous oxides; carbon disulphide; zinc, tin, arsenic, and bismuth sulphides; potassium ferrocyanide; urea; oxalic, tartaric, and citric acids and their salts. A blue coloration is produced by zinc and arsenic phosphides, and barium hypophosphite, and less marked blue colorations are obtained with lead sulphide or stannous chloride. A vigorous reaction attended by the development of a blue ring occurs with alcohol, ether, glycerol, and acetic acid. Iron and the ferrous compounds are very effective—*e.g.* iron, ferrous chloride, sulphate, oxalate, and sulphide—while the ferric compounds are inactive. The coloration which nitric oxide produces with cupric salts was observed by E. Desbassayns de Richemont, and that with ferrous salts by V. A. Jacquelain—*vide supra,* nitric oxide. O. Wentzky considers that the acid is strong enough to displace sulphuric acid from copper sulphate, forming **copper hydroxynitrosylsulphonic acid,** $O:(N.O.SO_3)_2:Cu$. The copper and ferrous compounds have been discussed in connection with the solubility of nitric oxide in ferrous and cupric salt soln. E. Scandola found that hydroxynitrosylsulphonic acid in contact with methyl, ethyl, propyl, isobutyl, or isoamyl alcohol gives a positive reaction; octyl alcohol gives an uncertain reaction, but at a higher temp. a blue coloration is formed, whilst cetyl alcohol does not react. Isopropyl and secondary butyl alcohols both give the reaction, but methyl alcohol forms a resin. Tertiary butyl and tertiary amyl alcohols react easily at the ordinary temp. without the formation of blue compounds, which seem to appear on heating the alcohols with amyl alcohol at 140°–150°. Glycerol, mannitol, erythritol, and many carbohydrates give the reaction; allyl alcohol forms only a brown resin. Lactic, malic, and tartaric acids react easily, citric acid with difficulty, whilst benzyl and cinnamyl alcohols become resinous. Nitroethane and butane give a positive, nitromethane a negative result; in the same way, nitrobenzene, nitrotoluene, and trinitrophenol do not react. The ethers behave like the alcohols; of the aldehydes only formaldehyde gives the reaction; others become resinous without turning blue. Chloral neither becomes resinous nor gives the reaction; acetone immediately gives a brown resin; the results were negative in the case of benzaldehyde and salicylaldehyde, also with formic, acetic, oxalic, benzoic, and cinnamic acids, but positive with the esters of the acids. Carbamide and uric acid give no reaction; phenol gives a reddish-brown to a bluish-green coloration, which is different from the lustrous colour of copper hydroxynitrosylsulphonate. Anisic acid gives the reaction. The mechanism of the formation of nitrosylsulphonic acid by the decomposition of alkyl nitrates and nitrites can be explained by a reaction between the ester and the acid which leads to the formation of alkyl sulphuric acids; these form addition or condensation products of nitric acid with the sulphonic acid.

P. Sabatier found that when nitric acid or nitrogen oxides are dissolved in sulphuric acid containing sulphur dioxide, and the soln. is exposed to moist air, there are indications of the formation of a dark blue compound. If a mixture corresponding with $4NO+O_2$ is passed into sulphuric acid, sat. with sulphur dioxide, and cooled at 0°, the liquid remains colourless, but when water is added very slowly, a dark blue soln. is formed. Similarly, when a mixture of air and nitric oxide is passed into monohydrated sulphuric acid, sat. with sulphur dioxide, and cooled to 0°, the bluish-violet soln. is formed at once with vigorous effervescence. With more conc. sulphuric acid, the liquid is at first colourless, and slowly develops the bluish-violet colour. It was thought by P. Sabatier that peroxylamidosulphonic acid was formed, but there is no real evidence of this. The blue acid decomposes spontaneously into sulphuric acid, sulphur dioxide, and nitric oxide, but it is more stable than E. Frémy's potassium peroxylamidodisulphonate, and does not decompose rapidly even at 100°.

When agitated with air or mixed with hydrogen dioxide, persulphuric acid, nitric acid, chlorine, or potassium chlorate, hydroxynitrosylsulphonic acid is rapidly decolorized. Potassium perchlorate and bromine act more slowly. Alkali chlorides are immediately decomposed with evolution of hydrogen chloride and chlorine; potassium iodide at once decolorizes the liquid, and iodine is liberated. Sulphurous acid is without action; water at once decomposes the blue compound. Most metallic oxides and carbonates decompose the soln. of nitrosodisulphonic acid, and are converted into sulphates. Ferric oxide, however, gives a wine-red soln., and the same compound is formed by placing metallic iron or a conc. soln. of ferrous chloride or sulphate, or some particles of ferrous oxalate into the acid. Ferric salts do not give this coloration. Cupric carbonate, oxide, or hydroxide, metallic copper, or any cuprous salt yields an intense blue-violet coloration. With copper or cuprous salts, nitric oxide is liberated. Chromic hydroxide also yields a very deep blue-violet soln., but chromium and chromous salts have no action. In all these cases, the colour of the soln. of the salts is very much more intense than that of the acid, and the soln. themselves are more stable. A soln. of nitrososulphonic acid or sodium nitrite in sulphuric acid is reduced not only by cuprous and ferrous salts, but also by a large number of other substances, with production of the blue nitrosodisulphonic acid. Mercury acts very rapidly, but also readily decomposes the nitrosodisulphonic acid. Finely divided silver, tin, and aluminium behave in the same way, and so also do cadmium, antimony, and lead, although much more slowly. Zinc, even in powder-form, bismuth, chromium, uranium, sulphur, phosphorus, nickel, arsenic, thallium, and magnesium react more or less readily, but do not produce the blue compound. Selenium and tellurium behave as with sulphuric acid alone. Arsenious anhydride, antimonous, manganous, and stannous oxides, mercurous and chromous chlorides, carbon bisulphide, and arsenic, bismuth, tin, and zinc sulphides, potassium ferrocyanide, carbamide, and oxalic, tartaric, and citric acids give no distinct result. On the other hand, the blue product is readily produced by zinc phosphide or arsenide, and by barium hypophosphite, less readily by lead sulphide and stannous chloride. Alcohol, ether, glycerol, and even acetic acid will produce a blue ring if added to the hydroxynitrosylsulphonic acid soln. The salts are more stable than the acid, and if a cupric salt or a ferric salt is dissolved in the nitrososulphonic acid soln. and the reducing agents are then allowed to act, the colour produced is much more intense, and it is observed with substances such as arsenic and zinc sulphides, bismuth, zinc powder, etc., which do not seem to act under ordinary conditions. Sulphur dioxide reduces the hydroxynitrosylsulphonic acid only in presence of water. The blue compound is formed, for instance, if sulphur dioxide is dissolved in sulphuric acid dil. with one-third of its vol. of water, and this liquid is added to an equal vol. of the hydroxynitrosylsulphonic acid soln. The copper salt is formed by adding copper nitrite to a soln. of sulphur dioxide in sulphuric acid containing a small quantity of water. P. Sabatier obtained unstable **lead nitrosylsulphonate,** $Pb(ON)(SO_3)_2$, by adding lead oxide, hydroxide, or carbonate to a blue soln. of the acid $NO(HSO_3)_2$. Much lead sulphate is precipitated. The salt is not stable in the presence of conc. sulphuric acid.

F. Raschig tried to prove that P. Sabatier's blue acid is the same as hydroxynitrosylsulphonic acid, and that when nitric oxide is passed into a soln. of copper sulphate, in conc. sulphuric acid, the product is



$$O{=}N<\begin{matrix}O\\SO_2\end{matrix}>Cu$$

He said that hydroxynitrosylsulphonic acid is produced by the action of sulphur dioxide on nitrous acid in 70 per cent. sulphuric acid as a direct product of the interaction of nitrous and sulphurous acids, and not by the reduction of chamber crystals—nitroxylsulphonic acid—because he supposed that the latter cannot exist in less than 80 per cent. sulphuric acid. This assumption was shown, by W. C. Reynolds and W. H. Taylor, to be unfounded; nitroxylsulphonic acid can exist in the presence of even 60 per cent. sulphuric acid. Further, the blue colour produced by the action of sulphurous acid, or other reducing agent, on a nitrite in the presence of a conc. sulphuric acid soln. of a copper salt, was supposed by F. Raschig to be the copper salt of P. Sabatier's acid, whereas, according to W. C. Reynolds and W. H. Taylor, the product is the complex which nitric acid forms with copper sulphate, and studied by W. Manchot, V. Kohlschütter, etc.—*vide supra*. The existence of F. Raschig's nitrosylsulphonic acid may therefore be questioned, and the same remark applies to his statement of the identity of P. Sabatier's blue acid with the product of the reaction of nitrous and sulphurous acids in the presence of a copper salt.

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§ 64. Nitroxylsulphonic Acid or Nitrosylsulphuric Acid

This compound was was first reported by F. Clément and C. B. Désormes[1] to be formed in the lead-chamber during the manufacture of sulphuric acid, and hence it is called *chamber-crystals* or *lead-chamber crystals*. F. Raschig called the compound *Nitrosulfosäure*, and it has also been called **nitrosylsulphuric acid,** regarded as constituted $NO.O(HSO_3)$; it can also be called **nitroxylsulphonic acid,** if it be constituted $HO.SO_2.NO_2$, or $NO_2(HSO_3)$. The former hypothesis is fashionable because it is the more probable one. The compound was synthesized by H. Davy, and was described by J. Dalton. V. Lenher and J. H. Mathews could not prepare **nitrosylselenic acid,** $HO.SeO_2.O.NO$; but they did get **dinitroxylselenyl,** $NO_2.SeO_2.NO_2$, or $SeO_2(O.NO)_2$, by the action of nitrogen peroxide on conc. selenic acid cooled by solid carbon dioxide. The dark blue solid melts at —13°, and decomposes above this temp. into nitrogen peroxide and selenic acid. J. Meyer and co-workers, however, prepared nitrosylselenic acid, $NO.O.SeO_2.OH$, by the action of a large excess of liquid nitrogen trioxide on ice-cold, anhydrous selenic acid. The colourless, snow-like mass melts with decomposition at 80°. It is somewhat unstable at atm. temp., and is decomposed by water.

Preparation of nitroxylsulphonic acid from sulphuric acid and nitrogen oxides.—G. Aimé, H. Rose, and F. Kuhlmann showed that anhydrous sulphuric acid absorbs nitric oxide. Nitroxylsulphonic acid is produced when conc. sulphuric acid is treated with one of the nitrogen oxides other than nitrous oxide. Thus, A. Bussy, F. H. de la Provostaye, O. Henry and A. A. Plisson, and C. A. Winkler used nitric oxide, or a mixture of nitric oxide and oxygen—but, according to J. J. Berzelius, and J. L. Gay Lussac, nitric oxide is not absorbed by the acid; C. Weltzien, dry nitrogen trioxide; J. L. Gay Lussac, A. Rose, and R. Weber, nitrogen peroxide: $N_2O_4+H_2SO_4=HNO_3+NO_2HSO_3$, and, added H. G. de Claubry, the formation of crystals is much accelerated if the vessel be filled with nitric oxide. A. Rose distilled a mixture of conc. nitric and sulphuric acids and obtained as a residue a soln. of nitrosylsulphonic acid in sulphuric acid, and M. Scanlan distilled a mixture of potassium nitrate in conc. sulphuric acid and obtained a crystalline mass towards the end of the operation. This was thought to be a potassium salt by the acid. He also found that if potassium nitrite be dissolved in sulphuric acid, the soln. has all the reactions of a soln. of nitroxylsulphonic acid in sulphuric acid. G. B. Taylor and co-workers represent the reaction: $2NO_2+H_2SO_4=HNO_3+NOHSO_4$. According to A. Sanfourche, a mixture of equimolar proportions of nitric oxide and nitrogen peroxide behaves towards sulphuric acid like nitrogen trioxide. Although the proportion of the trioxide actually formed is small, yet it serves as an intermediate compound in the soln.: $NO+NO_2=N_2O_3$; and $N_2O_3+2H_2SO_4=H_2O+2(NO.HSO_4)$.

Preparation from sulphur trioxide, nitrogen oxides, and water.—J. W. Döbereiner obtained nitroxylsulphonic acid by bringing the vap. of sulphur trioxide in contact with fuming nitric acid; H. G. de Claubry obtained it from a mixture of sulphur trioxide, nitrogen peroxide, and a little water; and F. Kuhlmann, by allowing monohydrated nitric acid, cooled by a freezing mixture, to absorb the vap. of sulphur dioxide. When the liquid thus obtained is distilled, it first evolves oxygen and nitrogen peroxide, and afterwards a sublimate of white needles collects, and the residue is a soln. of nitroxylsulphonic acid in sulphuric acid.

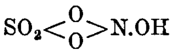
Preparation from a mixture of sulphur dioxide, nitrogen oxides with or without oxygen, and a little water.—G. Lunge found that nitric oxide and sulphur dioxide do not react at 100°, and that the two gases react in the presence of water and in the absence of oxygen, so that in a few hours the nitric oxide is all reduced to nitrous oxide, but not to nitrogen; but if dil. sulphuric acid, sp. gr. 1·32, is employed instead of water, the reduction does not occur; instead, the nitric oxide, sulphur dioxide, and water react to form nitroxylsulphonic acid. According to H. Davy, a mixture of sulphur dioxide, nitrogen peroxide, and water produces crystals of nitroxylsulphonic acid; but sulphur dioxide has no action on nitric oxide, nor on nitrogen peroxide vap. so long as water is not present—the admission of a trace of water then leads to the formation of the crystals of nitroxylsulphonic acid. C. A. Winkler also said that nitrogen peroxide and sulphur dioxide in an atm. of carbon dioxide react only in the presence of moisture. H. Reinsch observed the formation of crystals of nitroxylsulphonic acid when a mixture of sulphur and potassium nitrate (1 : 3) is inflamed under a large bell-jar. According to H. G. de Claubry, liquid sulphur dioxide mixes, but does not react with liquid nitrogen peroxide at —20°, but on the addition of a single drop of water, there is a violent disengagement of gas attended by the formation of crystals of nitroxylsulphonic acid. The crystals can be washed with liquid nitrogen peroxide, and dried in vacuo or in a stream of air at 20°–30°. The reaction was also studied by F. H. de la Provostaye, R. Müller, and G. Lunge and E. Berl. If a mixture of dried nitrogen peroxide and sulphur dioxide be passed into a large flask whose interior is moistened with a layer of conc. sulphuric acid, crystals of this acid are formed. F. Sestini also noticed that if sulphur dioxide be dropped into nitric acid, red fumes are evolved and crystals of nitroxylsulphonic acid are formed; and R. Weber prepared the acid by passing sulphur dioxide into well-cooled fuming nitric acid until a mush of crystals is formed, but not until the nitric acid is all decomposed. The crystals are dried on porous tiles over conc. sulphuric acid. W. A. Tilden made nitroxylsulphonic acid by leading nitrosylchloride (by heating aqua regia) into conc. sulphuric acid.

Analyses in agreement with the empirical formula $NO_2.HSO_3$ were made by W. Henry, H. G. de Claubry, T. Thomson, C. Weltzien, R. Müller, and R. Weber. The products obtained by several different methods of preparation were found by G. A. Elliott and fellow-workers to furnish a substance with the same crystalline form, and m.p. Fractional crystallization from sulphuric acid did not effect any change. Hence, the existence of non-dynamic isomerides is improbable, although the acid may be tautomeric. F. Raschig preferred the formula *nitrosylsulphuric acid*, $O:N.O.SO_2.OH$, to *nitroxylsulphonic acid*, $HO.SO_2.NO_2$, since, as C. A. Michaelis and O. Schumann showed, it reacts with phosphorus pentachloride: $NO.O.HSO_3+PCl_5=H(Cl)SO_3+NOCl+POCl_3$; and, according to C. A. Girard and J. A. Pabst, with sodium chloride, or bromide, forming the respective nitrosyl halide. The analogies with $NH_2OH+HO.HSO_2=NH_2.SO_2.OH+H_2O$, and $HO.NO_2+HO.HSO_2=H_2O+NO_2.HSO_3$, also favour the $NO.O.HSO_3$ formula. He also cited as evidence in favour of this formula the oxidation of hydroxyimidomonosulphonic acid by Caro's acid to form hydroxynitrosylsulphonic acid (*q.v.*). According to L. H. Milligan and G. R. Gillette, nitroxylsulphonic acid made from nitrous and sulphuric acids: $HNO_2+H_2SO_4\rightleftharpoons NOHSO_4+H_2O$, may be regarded as nitrous acid stabilized by soln. in conc. sulphuric acid; for when solid nitrosylsulphuric acid crystallizes from the soln., it is simply that the system has become supersaturated with respect to this particular compound, under the conditions of the experiment. The dilution of the sulphuric acid with water decreases the stability of the nitrosylsulphuric acid; nitrous acid is re-formed, and is decomposed at least partially into nitric oxide and nitric acid. G. Lunge and E. Berl said that the formation of the acid from sulphur dioxide and nitric acid favours the nitroxyl formula; while its formation from sulphuric acid and nitrogen trioxide favours the nitrosyl formula. In many of its reactions, the acid behaves like a nitrosyl-compound. W. A. Tilden showed that the crystallized acid furnishes nitrosyl chloride and sulphuric acid when treated with hydrogen chloride at ordinary temp. The reaction is reversible. This agrees with the assumption that the acid contains the nitrosyl-group, and this is more definitely suggested by the reaction between the acid and benzoyl chloride, producing according to G. A. Elliott and co-workers, dibenzoylsulphuric acid, $SO_2(O.CO.C_6H_5)_2$, the formation of which can be explained only on the assumption that the acid contains both a hydroxyl and nitrosyl group. The first stage of the reaction can be symbolized: $HO.SO_2.O.NO+C_6H_5CO.Cl=NOCl+HO.SO_2.O.CO.C_6H_5$, and the second stage: $C_6H_5CO.Cl+HO.SO_2.O.CO.C_6H_5=HCl+C_6H_5.CO.O.SO_2.O.CO.C_6H_5$. The action of acetyl chloride, and of acetic anhydride investigated by A. J. van Peski, yielded similar evidence. G. A. Elliott found that nitroxylsulphonic acid reacts with ether, producing ethyl nitrate, and hydrosulphate: $(C_2H_5)_2O+HO.SO_2.O.NO=C_2H_5.HSO_4+C_2H_5.O.NO$; ethyl hydrosulphate and soln. of nitroxylsulphonic acid gave no nitroethane as would be expected to result if the acid had the NO_2-structure. G. A. Elliott and co-workers agree with J. Biehringer and W. Borsum that both *p*-nitro- and *p*-nitrosodimethylaniline are produced by the action of a sulphuric acid soln. of dimethylaniline on solid sodium nitrite; and they observed in addition that (i) the percentage yield of the *p*-nitro-derivative increases with the excess of nitroxylsulphuric acid used in the reaction mixture. (ii) If an excess of dimethylaniline is used, no oxides of nitrogen are produced by pouring the mixture on ice and no *p*-nitro-derivative is obtained. (iii) When an excess of nitroxylsulphuric acid is present, and the mixture is poured into absolute alcohol or dry ether, no *p*-nitro-derivative is obtained. Both these solvents rapidly decompose nitroxylsulphuric acid, forming ethyl nitrite and ethyl hydrogen sulphate.

(iv) When crystalline nitroxylsulphuric acid is added to a soln. of dimethylaniline in dil. sulphuric acid (2*N*-), in which the former acid is immediately decomposed, both the *p*-nitro- and the *p*-nitroso-derivative are obtained. (v) If a soln. of dimethylaniline in conc. sulphuric acid is added to a dil. soln. of nitric acid (10 per cent.) or of potassium nitrite (5 per cent.), the *p*-nitro-derivative is formed. (vi) No sulphur dioxide could be detected in any of the experiments. All these facts are in accord with the view that the *p*-nitrodimethylaniline is not produced by the action of a presumed nitrosulphonic acid, but is a secondary product obtained by pouring the reaction mixture on ice, and is produced either by secondary oxidation of the nitroso-compound or by direct nitration of the dimethylaniline. The results of J. Biehringer and W. Borsum do not establish, therefore, the existence of nitroxylsulphonic acid or the possibility of tautomerism.

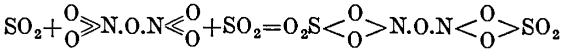
The fact that no salts—**nitroxylsulphonates**—have been prepared from nitroxylsulphonic acid might serve as an argument that it is not an acid at all. C. Schultz-Sellack obtained what can be regarded as **potassium nitroxylsulphonate,** $KSO_3.NO_2$, or $KO.SO_2.O.NO$, so far as mere composition goes, by the action of dry liquid sulphur dioxide on potassium nitrate; it is decomposed by a trace of water. There is no definite evidence of the conversion of the acid into **nitroxylsulphonic anhydride,** $(NO.O.SO_2)_2O$, although E. Berl said that it is formed by the action of nitric oxide on sulphur trioxide, or of sulphur dioxide on well-cooled nitrogen pentoxide.

While favouring the formula $HO.SO_2.O.NO$ rather than $HO.SO_2.NO_2$, G. A. Elliott and co-workers said that the structure



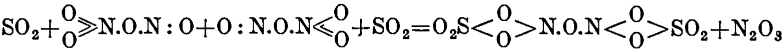
$$SO_2<^{O}_{O}>N.OH$$

merits consideration, because (i) an acid of this type would lose water on heating to give an anhydride of the structure $SO_2=O_2=N.O.N=O_2=SO_2$, a change which is parallel to the conversion of nitric acid into nitrogen pentoxide. (ii) It offers an explanation of the great difficulty of replacing both the hydroxyl groups of sulphuric acid by the nitroso-group. (iii) The structure is in accord with the methods of synthesis of the acid. (iv) The behaviour of the acid on reduction is more in accord with this structure than with the nitroso-structure. (v) The synthesis of the anhydride from sulphur dioxide and nitrogen pentoxide, observed by E. Berl, is readily explicable in terms of the above formula:



$$SO_2+{}^{O}_{O}\geqslant N.O.N\leqslant^{O}_{O}+SO_2=O_2S<^{O}_{O}>N.O.N<^{O}_{O}>SO_2 \quad \text{(iii)}$$

and so is the production of the anhydride from nitrogen tetroxide and sulphur dioxide observed by F. G. de la Provostaye, in which reaction nitrogen trioxide is a by-product:



$$SO_2+{}^{O}_{O}\geqslant N.O.N:O+O:N.O.N\leqslant^{O}_{O}+SO_2=O_2S<^{O}_{O}>N.O.N<^{O}_{O}>SO_2+N_2O_3$$

J. Biehringer and W. Borsum suggested that nitrosylsulphuric acid exists in two tautomeric forms, $HO.SO_2.O.NO \rightleftharpoons HO.SO_2.NO_2$, which are in equilibrium in conc. sulphuric acid soln. and in the molten state. In support of this, they found that in some cases it can react simultaneously as two different acids, for, when a soln. of dimethylaniline in conc. sulphuric acid is slowly treated with the requisite amount of sodium nitrite, both *p*-nitrodimethylaniline and *p*-nitrosodimethylaniline are produced, the former represents the nitrosyl-acid and the latter the nitroxyl-acid. At 10° to 15°, the yields are respectively 8·33 and 7·45 per cent., and at 28° to 30°, 42·85 and 39·33 per cent. This shows that the nitrosyl-form of the acid is favoured at the higher temp.

J. L. Gay Lussac described the crystals as four-sided prisms; G. A. Elliott and co-workers, and R. Müller, as rhombic prisms; and F. H. de la Provostaye, as colourless, transparent, laminated, feathery, or granular masses of crystals. C. Weltzien said the acid melts at 73° giving off red vapours; and G. A. Elliott and co-workers said that the rhombic prisms melt at 73·5°; while W. A. Tilden gave 85°–87° for the m.p. F. H. de la Provostaye found that an oily liquid is produced when the acid is heated, and the more the crystals are contaminated with sulphuric acid the lower the m.p. Fusion occurs at 60°, and the liquid may be under-cooled to 10°, and it then solidifies when shaken, and much heat is evolved, which, according to W. Henry, T. Thomson, and H. G. de Claubry, causes the acid to decompose. The last-named also found that at 50°, the crystals begin to give off nitric oxide and nitrogen peroxide; the remaining solid softens at 100° and fuses between 120° and 130°, disengaging at the same time much nitrogen peroxide; at 200° a little nitric acid is also given off; at 280°, nitric acid is still evolved and the yellowish-red liquid is transparent; and at 357°, nearly colourless sulphuric acid collects as a distillate which gives off nitric oxide when treated with water. W. Henry said the crystals do not decompose at 104·4°, and they give off gas at 138°. These various statements are so much at variance that if the thermometers were right, the compounds tested were chemically different. C. A. Michaelis and O. Schumann considered that dinitrosylpyrosulphuric acid is formed at an intermediate stage in the thermal decomposition of nitroxylsulphonic acid: $NO_2.SO_2.\boxed{OH+H}O.SO_2.NO_2 \rightleftharpoons NO_2.SO_2.O.SO_2.NO_2+H_2O$. G. A. Elliott added that the reaction $NO.O.SO_2.OH+NO.O.SO_2.OH \rightleftharpoons NO.O.SO_2.O.SO_2.OH+HNO_2$ is also possible, but the change in the nitrous acid content of the system favours the former hypothesis. H. I. Schlesinger and A. Salathe studied the absorption spectrum of nitroxyl sulphuric acid. G. B. Taylor and co-workers represented the result of electrolyzing nitroxylsulphonic acid in a partitioned cell by: $NOHSO_4+2H_2O=HNO_3+H_2SO_4+H_2+2$ farads. In practice, the nitric acid or nitroxysulphonic acid diffuses through the diaphragm, and is reduced to nitric oxide and some free nitrogen.

W. Henry said that nitroxylsulphonic acid stains the skin yellow. G. Lunge and E. Berl discussed the possible *rôle* played by this compound as a carrier of oxygen in the manufacture of sulphuric acid by the chamber process. The crystals rapidly dissolve in **water** with the disengagement of heat, and the evolution of nitric oxide, and there remains sulphuric acid with much nitric oxide in soln.—the gas is expelled by boiling the liquid, but in air, some nitric oxide is converted into nitrogen peroxide which forms nitric acid—according to W. Henry; and both nitric and nitrous acids, according to H. G. de Claubry. If air be excluded, A. Rose, and T. Thomson showed that the sulphuric acid is free from nitric acid. C. F. Rammelsberg and J. Philipp represented the reactions by: $16NO_2HSO_3+9H_2O=16H_2SO_4+4NO+2HNO_3+5N_2O_3$, an equation which looks more like an algebraic exercise than a representation of a chemical process. According to G. Lunge, nitrous acid is first formed: $NO_2HSO_3+H_2O=H_2SO_4+HNO_2$; the nitrous acid then decomposes: $3HNO_2=HNO_3+2NO+H_2O$; and if a very small proportion of water is used, $2NO_2HSO_3+H_2O=2H_2SO_4+N_2O_3$. According to S. L. Dana, less red vapours are developed if the reaction occurs in an atm. of an inert gas—carbon dioxide, hydrogen or nitrogen—and the soln. appears at first blue, then green, and lastly yellow. When the crystals are laid on snow, they melt, and sinking in the snow, impart to it a dark blue colour, while the temp. may fall down to −26·7°, when no further action takes place. C. A. Girard and J. A. Pabst's observations on the action of **sodium chloride and bromide** have been discussed above. J. W. Döbereiner showed that when the soln. of nitroxylsulphonic acid in sulphuric acid is distilled with **sulphur,** it yields nitric oxide, sulphur dioxide, and a white sublimate; and when treated with **hydrogen sulphide,** sulphur with a red colour is first precipitated, the colour then turns yellow, and sulphur dioxide is rapidly evolved. E. Frémy said that **sulphur dioxide** decomposes the crystals of nitroxysulphonic acid, forming nitrous oxide; and, according to R. Weber, the soln. of nitroxylsulphonic acid in sulphuric acid is partly decomposed by that gas, and G. Lunge represents the reaction: $2NO_2HSO_3+SO_2+2H_2O \rightleftharpoons 2NO+3H_2SO_4$. E. Sorel found that at a high temp., with a deficiency of oxygen and an excess of water, nitroxylsulphonic acid is reduced, while at a low temp., with plenty of oxygen, and conc. acid, nitroxylsulphonic acid is formed. The solubility of nitroxylsulphonic acid in **sulphuric acid** was observed by J. W. Döbereiner, J. J. Berzelius, R. Weber, S. L. Dana, and R. Müller. The solubility is greater the more conc. the sulphuric acid, and increases with the temp., so that by cooling the hot sat. soln. crystals separate out, and R. Müller found that they are but slightly decomposed. G. A. Elliott and co-workers found that the solubility, *S* grms. of nitroxylsulphonic acid per 100 grms. of soln., in sulphuric acid containing *p* per cent. H_2SO_4, is:

	p . . .	56·7	62·1	73·1	74·9	84·1	90·4	99·8
S at	0·0° .	—	11·9	17·3	19·7	30·5	35·1	—
	20·0° .	19·3	22·6	27·0	31·4	42·4	49·2	62·0
	37·3° .	29·9	34·3	39·4	40·8	50·2	58·5	66·1
	49·6° .	35·6	39·3	46·0	46·2	56·5	61·6	67·8

G. Lunge and E. Weintraub showed that when nitrogen peroxide is mixed with sulphuric acid, nitroxylsulphonic acid and nitric acid are formed, but since the reverse change may also occur, the mixture contains all four compounds, and a state of equilibrium is attained. (1) When sulphuric acid of sp. gr. 1·84 is employed, the conversion of nitrogen peroxide into nitroxylsulphonic and nitric acids is the main reaction, the reverse reaction only coming into prominence when the quantity of sulphuric acid is small. (2) The affinity of sulphuric acid for nitric peroxide decreases rapidly as the amount of water is increased, hence with sulphuric acid of sp. gr. 1·65 a large proportion of the peroxide remains uncombined, although the quantity of nitric acid present is small. (3) In the manufacture of sulphuric acid, the nitrogen peroxide is almost completely converted into nitroxylsulphonic acid and nitric acid, owing to the presence of a large excess of sulphuric acid, and similarly, nitrous fumes are completely absorbed by a large excess of sulphuric acid. R. Weber showed that the soln. of nitroxylsulphonic acid in sulphuric acid can be distilled without losing nitrous acid. G. Lunge also made some observations on this subject. G. A. Elliott and co-workers did not succeed in dehydrating nitroxylsulphonic acid by cooling a sat. soln. in 98 per cent. sulphuric acid at 50°. Nitroxylsulphonic acid, indeed, can exist in sat. soln. in sulphuric acid at 300°. This is remarkable in view of the loss of water when sulphuric acid alone is heated. H. I. Schlesinger and A. Salathe measured the absorption spectrum of sulphuric acid soln. of nitroxylsulphonic acid. T. Thomson observed that no decomposition occurs when nitroxylsulphonic acid is triturated with **ammonium carbonate**; and J. Pelouze, that **ammonium sulphate** reacts with a soln. of nitroxylsulphonic acid in conc. sulphuric acid at 160°, giving off nitrogen gas. J. W. Döbereiner found that with the same acid menstruum at 62° **phosphorus** inflames with the emission of red sparks. G. A. Elliott and co-workers found that with **phosphorus pentoxide**, no anhydride is formed—nitroxylsulphonic acid is the main product, being probably formed by a recombination of the products of decomposition during the distillation. C. A. Michaelis and O. Schumann's observations on the action of **phosphorus pentachloride** have been already described.

H. G. de Claubry found that when nitroxylsulphonic acid is heated with **mercury,** there is formed mercuric sulphate, sulphur dioxide, nitric oxide, and nitrogen; and G. Lunge said that when a soln. in conc. sulphuric acid is shaken with mercury, nitric oxide and sulphuric acid are quantitatively formed; and F. Raschig observed that the reaction is completely inhibited by mercury, possibly with the formation of hydroxynitrosylsulphonic acid. A. Graire found that the acid is not reduced further than nitric oxide by agitation with mercury; but if sulphur dioxide is present, some nitrous oxide may be formed. J. W. Döbereiner found that a soln. of nitroxylsulphonic acid in conc. sulphuric acid oxidizes mercury; **copper, silver, zinc,** and **iron,** and the liquid is coloured red, violet-blue, or purple; and J. J. Berzelius added that nitric oxide is at the same time evolved. J. W. Döbereiner also found that **ferrous sulphide** is coloured a bright red. H. G. de Claubry showed that when nitroxylsulphonic acid is treated with **manganese oxide,** the solid becomes red-hot; and with **barium oxide,** the reaction is more vigorous, forming barium mono- and di-oxides, sulphate, and nitrate; while J. W. Döbereiner found that when **potassium hydroxide, calcium oxide,** or **magnesium oxide** is mixed with a soln. of nitroxylsulphonic acid in sulphuric acid, much heat is evolved, and nitric oxide is vigorously evolved; with **potassium nitrate,** there is much frothing, and nitrogen peroxide is given off. T. Thomson showed that when nitroxylsulphonic acid is triturated with **potassium hydrocarbonate,** nitric oxide is evolved which gives red fumes in air, and finally a mush is produced which contains the alkali carbonate, sulphate, and a trace of nitrate. J. W. Döbereiner observed that a soln. of nitroxylsulphonic acid in sulphuric acid is decomposed by **alcohol, ether, sugar, or starch.**

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§ 65. Nitrosyl and Nitroxyl Compounds of Pyrosulphuric Acid

H. Rose,[1] G. Aimé, and F. Kuhlmann showed that sulphur trioxide absorbs nitric oxide, forming **dinitrosylpyrosulphuryl,** $N_2O_3.2SO_3$, or $NO.O.S_2O_5.O.NO$, according to A. Brüning, $3SO_3+2NO=SO_2+N_2O_3.2SO_3$. A. Morren claimed to have obtained the same product by passing a silent discharge through a dry mixture of oxygen, nitrogen, and sulphur dioxide; and M. Chevrier, and M. Berthelot obtained it by the action of the electric discharge on a mixture of sulphur vapour and nitrous oxide. According to F. H. de la Provostaye, when a mixture of liquid sulphur dioxide and nitrogen peroxide is sealed in a glass tube at ordinary temp., heat is evolved, and a greenish liquid is formed which deposits crystals of this compound. When the tube is opened, an explosion occurs unless the tube is surrounded by a freezing mixture. No reaction occurs between the liquids under atm. press. When sulphur trioxide is brought in contact with a liquid mixture of sulphur dioxide and nitrogen peroxide, this compound is immediately formed. G. Lunge and E. Berl consider that the product of the reaction between liquid sulphur dioxide and nitrogen peroxide is not this substance at all, but hydroxynitroxysulphonic acid—*vide supra*. R. Weber obtained dinitrosylpyrosulphuryl by heating nitrosylnitroxypyrosulphuryl—*vide infra*; and C. A. Michaelis and O. Schumann said that it is formed in an intermediate stage of the decomposition of nitroxylsulphonic acid.

F. H. de la Provostaye reported that the crystals consist of regular, rectangular prisms with the opposite lateral edges truncated; or a white mass of silky needles. The sp. gr. is 2·14. A. Brüning found the m.p. to be 217°, and F. H. de la Provostaye said that the compound begins to melt at 217°, and becomes quite fluid at 230°. The fused mixture near its b.p. is yellowish-red; on cooling to 230°, it is yellow; and it begins to solidify at 217°. The solid is transparent at 190°, and below this temp. it appears opaque and greenish-yellow, and is white when cold. The b.p. is 357·3°, the same as mercury, and it sublimes without decomposition. H. Rose added that the hard white solid does not fume in air. F. H. de la Provostaye said that it stains the skin at first dark red, then yellow, and then slightly blackish. A. Brüning, and H. Rose found that the compound attracts moisture from the air, and loses some nitrogen trioxide; H. Rose, and R. Weber said that the compound dissolves rapidly in water, forming sulphuric and nitric acids with the evolution of nitric oxide; aq. soln. of salts and alkalies act very much like water. H. Rose found it to dissolve freely in cold conc. sulphuric acid; but F. H. de la Provostaye said that it does not dissolve in the cold acid, and only slowly in the hot conc. acid, from which soln., crystals of nitroxylsulphonic acid are deposited. The compound fuses in a current of ammonia, there is a great rise of temp., and a yellowish mass is formed which becomes white ammonium sulphate; with the fused compound ammonia forms ammonium hydrosulphate with the evolution of nitrogen: $N_2O_3.2SO_3+4NH_3=2NH_4HSO_4+2N_2+H_2O$. Dry barium oxide does not act on the compound at ordinary temp., but when heated the mass becomes incandescent, forming barium sulphate with the evolution of red fumes; mercury, also, has no action at ordinary temp., but when heated, mercuric sulphate is formed with the evolution of nitric oxide and sulphur dioxide. H. Rose found it converts alcohol into ethyl nitrite without forming red fumes.

According to R. Weber,[2] if a slow current of the vapour of sulphur trioxide be passed into cold hydrated nitric acid, a solid mass of crystals of **mononitrosylpyrosulphuric acid,** $HO.S_2O_6(NO_2).H_2O$, is produced. The crystals can be drained and dried on a porous tile over conc. sulphuric acid. The colourless crystals are very deliquescent; they give off brown fumes when heated, and a sublimate of nitroxylsulphuric acid. They dissolve in water, forming sulphuric and nitric acids. No salts have been reported. A. Hantzsch and L. Wolf regard this product as *nitronium pyrosulphate*, $\{NO(OH)_2\}.HS_2O_7$, or $\{N(OH)_3\}.S_2O_7$. G. Oddo and A. Casalino obtained **nitrosylpyrosulphuryl,** $NO.O.SO_2{-}O{-}SO_2.O.NO$, by the action of sulphur trioxide on nitrogen peroxide (*q.v.*).

R. Weber[3] also reported what has been regarded as **nitrosylnitroxylpyrosulphuryl,** $N_2O_4.2SO_3$, or $NO.S_2O_7.NO_2$, to be formed by passing nitrogen peroxide into anhydrous sulphuric acid; if a rise of temp. is prevented, when the acid is sat., a white crystalline mass is formed which with a stronger heating gives off oxygen and produces dinitrosylpyrosulphuryl. R. Weber suggested that the product may be a mixture of $N_2O_3.2SO_3$ and $N_2O_5.2SO_3$.

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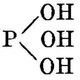
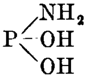
§ 66. Derivatives of Amidophosphorous and Amidophosphoric Acids

The ammonia derivatives of phosphorous acid can be conveniently regarded as substitution products obtained when the amido- or NH_2-group replaces the hydroxyl group of the parent phosphorous acid:



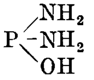
$$P{<}\begin{matrix}OH\\OH\\OH\end{matrix}$$

Phosphorous acid.



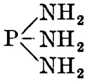
$$P{<}\begin{matrix}NH_2\\OH\\OH\end{matrix}$$

Monamidophosphorous acid.



$$P{<}\begin{matrix}NH_2\\NH_2\\OH\end{matrix}$$

Diamidophosphorous acid.

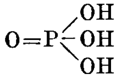


$$P{<}\begin{matrix}NH_2\\NH_2\\NH_2\end{matrix}$$

Phosphorous triamide.

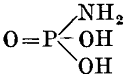
The *monamidophosphorous acid* has not been obtained; but **diamidophosphorous acid,** $(NH_2)_2POH$, was made in 1891, by T. E. Thorpe and A. E. H. Tutton,[1] by the action of ammonia on a soln. of phosphorous oxide in ether or benzene. The reaction is symbolized: $P_4O_6+8NH_3=4(NH_2)_2P(OH)+2H_2O$, followed by $2H_2O+(NH_2)_2P(OH)=(NH_4O)_2P(OH)$; or summating the two equations: $P_4O_6+8NH_3=(NH_4O)_2P(OH)+3(NH_2)_2P(OH)$. The product is a white solid which when heated in a test-tube gives off ammonia, and then fuses and sublimes. It dissolves in water with such great violence that the mass becomes incandescent. When treated with hydrochloric acid, ammonium chloride and phosphorous acid are formed; the reaction can be symbolized: $HO.P(NH_2)_2+2HCl+2H_2O=2NH_4Cl+P(OH)_3$, but the heat of the reaction is so great that the compound is partially resolved into phosphorus, phosphoric acid, and phosphine, which does not inflame spontaneously on exposure to the air. The substituted ammonias also react with the ethereal soln. of phosphorous oxide, forming the corresponding substituted diamides. *Phosphorous triamide*, or the normal *phosphorous amide*, has been previously discussed.

The following series of **amidophosphoric acids** has been reported:



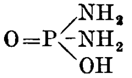
$$O{=}P{<}\begin{matrix}OH\\OH\\OH\end{matrix}$$

Phosphoric acid.



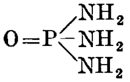
$$O{=}P{<}\begin{matrix}NH_2\\OH\\OH\end{matrix}$$

Monamidophosphoric acid.



$$O{=}P{<}\begin{matrix}NH_2\\NH_2\\OH\end{matrix}$$

Diamidophosphoric acid.



$$O{=}P{<}\begin{matrix}NH_2\\NH_2\\NH_2\end{matrix}$$

Phosphoric triamide.

Diamidophosphoric acid was found by H. N. Stokes[2] to unite with the elements of water, or rather with the bases, forming a series of salts of a pentabasic acid, **trihydroxydiamidophosphoric acid,** $(NH_2)_2P(OH)_3$, in which the amido-groups can play a similar *rôle* to that of hydroxyl, because their hydrogen atoms can be replaced by a metal. If silver diamidophosphate, $(NH_2)_2PO.OAg$, be treated with potassium hydroxide, a colourless, gelatinous mass, possibly **dipotassium silver trihydroxydiamidophosphate,** $(NH_2)P(OK)_2(OAg)$, is formed. This substance furnishes needle-like crystals of **potassium disilver trihydroxydiamidophosphate,** $(NH_2)_2P(OK)(OAg)_2$. When these crystals are washed with ice-cold water, they decompose, forming potassium diamidophosphate and **trisilver trihydroxydiamidophosphate,** $(NH_2)_2P(OAg)_3.2H_2O$. The yellow compound loses its water of crystallization at 100°, and it then appears orange-red. It is immediately decomposed by boiling water, forming a reddish-brown amorphous mass which, after boiling a few minutes, consists of **tetrasilver hydrotrihydroxydiamidophosphate,** $P(NHAg)_2(OAg)_2(OH)$. If gelatinous dipotassium silver trihydroxydiamidophosphate be mixed with water, and treated with carbon dioxide, in the cold, a yellowish-red flocculent substance, resembling ferric hydroxide, separates out. After washing by decantation with water, and drying over sulphuric acid in vacuo, for a few days, the red powder has a composition the same as that of the preceding salt, but is thought to be **tetrasilver trihydroxydiamidophosphate,** $P(NH_2)(NHAg)(OAg)_3$. When freshly made, it may be the same as the preceding salt. The freshly prepared salt does not change under cold water, but in boiling water it forms a compact powder which is almost black and which does not detonate by friction. The powder which has been drying for some days over sulphuric acid detonates when heated, exhibiting a reddish flame and giving off ammoniacal fumes. If treated with conc. sulphuric acid the mass inflames; and boiling water converts it into a red powder which contains more phosphorus and silver than the original salt. If gelatinous dipotassium silver trihydroxydiamidophosphate be diluted with water to which 2 or 3 per cent. of potassium hydroxide has been added, and boiled, the soln. becomes red, then turbid, and deposits a dark brown mass, which is washed by decantation with boiling water, and digestion with a 2–3 per cent. soln. of potassium hydroxide, then washed with boiling water, by suction, and dried over sulphuric acid. The product is **pentasilver trihydroxydiamidophosphate,** $P(NHAg)_2(OAg)_3$. It explodes very readily by friction, by heat, or by treatment with conc. sulphuric acid.

H. N. Stokes prepared **monamidophosphoric acid,** $(NH_2)PO(OH)_2$, by hydrolyzing diphenylamidophosphate, $(NH_2)PO(OC_6H_5)_2$, with a soln. of potassium or sodium hydroxide; by the action of ammonia on silver phosphate; by hydrolyzing the product of the action of ammonia on diethylmonochlorophosphate; and by the action of nitrous acid on diamidophosphoric acid. The acid is best obtained by converting the alkali salt into the lead salt, which is then suspended in water at 0°, and treated with hydrogen sulphide. The clear filtrate is mixed with five times its vol. of alcohol, and the acid is precipitated as a mass of tabular, or anisotropic, cubic crystals. The acid has also been called *phosphamic acid,* and *phosphamidic acid.* Monamidophosphoric acid is readily soluble in water, but insoluble in alcohol. The aq. soln. has a sweetish taste; and gradually changes into ammonium dihydrogen phosphate. The change is rapid in hot soln. The first sign of change is the white precipitate which is formed when silver nitrate is added to the soln. The aq. soln. does not give ammonia when heated with alkali-lye. The dibasic acid forms two series of salts, $MH(NH_2)PO_3$, and $M_2(NH_2)PO_3$. The salts are produced when soln. of the metal salts are added to the alkali salt soln. In aq. soln., the salt passes slowly into an ordinary phosphate. With phenolphthalein, methyl-orange, or litmus as indicator there is no sharp change during the passage from the free acid to the neutral salt.

H. N. Stokes, and A. Sabanéeff prepared **ammonium hydromonamidophosphate,** $(NH_2)PO(OH)(ONH_4)$, by the action of ammonium sulphide on the acid or neutral silver salt, followed by precipitating the clear soln. with alcohol; also by adding alcohol to a soln. of the normal ammonium salt. The acicular crystals are stable, but decompose at 120° without melting—the residue melts at about 305°. A. Sabanéeff found the f.p. of aq. soln. of the salt agree with the simple formula, and the salt is structurally isomeric with hydrazine phosphite, $N_2H_4.H_3PO_3$. The normal salt, **ammonium monamidophosphate,** $(NH_2)PO(OH)(ONH_4)$, may exist in ammoniacal soln., but it decomposes into the acid salt when the attempt at its isolation is made. H. N. Stokes, and A. Sabanéeff obtained **hydroxylamine hydromonamidophosphate,** $(NH_2)PO(OH)(ONH_2.OH)$, by the action of hydroxylamine monochloride on potassium hydromonamidophosphate. The rhombic plates and prisms are sparingly soluble in water. The salt decomposes at about 95° with the evolution of gas; and changes easily when kept. A. Sabanéeff found the salt to be a structural isomer of hydrazine orthophosphate, $N_2H_4.H_3PO_4$.

H. N. Stokes prepared **lithium monamidophosphate,** as a crystalline powder, by precipitation from a soln. of the potassium salt on the addition of a lithium salt. When boiled with water, it furnishes lithium phosphate. He also made **sodium monamidophosphate,** $(NH_2)PO(ONa)_2$, by the action of sodium hydroxide on the acid salt. The acicular or prismatic crystals are not hygroscopic; they are very soluble in water; and alcohol precipitates the salt as an oily liquid from its aq. soln. The salt is decomposed by carbon dioxide into sodium carbonate and the acid salt. The acid salt or **sodium hydromonamidophosphate,** $(NH_2)PO(OH)(ONa)$, is obtained by boiling diphenylamidophosphate for 10 minutes with a conc. soln. of sodium hydroxide, and acidifying the ice-cold soln. with acetic acid. The precipitate which gradually forms is washed with alcohol, dissolved in aq. ammonia, and again precipitated with acetic acid. The powder consists of hexagonal plates or prisms; it is sparingly soluble in cold water; and insoluble in alcohol. The salt is slowly hydrolyzed to the phosphate by cold water, and rapidly by hot water or dil. acids. When heated, the salt loses ammonia, leaving a glassy mass of hexametaphosphate. The salt is precipitated from an ammoniacal soln. by the passage of carbon dioxide, or by driving out the ammonia with a current of air. There is possibly a small proportion of water of crystallization which does not hydrolyze the salt at 100°, but does so at 150°. H. N. Stokes made **potassium monamidophosphate,** $(NH_2)PO(OK)_2$, from the free acid and the alkali-lye. It is very soluble in water, and is not perceptibly hydrolyzed by water. He also made **potassium hydromonamidophosphate,** $(NH_2)PO(OH)(OK)$, by a method similar to that used for the sodium salt. The rhombohedral crystals are very soluble in cold water. The aq. soln. has a neutral reaction, and is slowly decomposed into phosphate when cold; the change is rapid with hot soln. When the salt is heated, ammonia is evolved, and potassium metaphosphate remains. If the ammoniacal soln. in the acid salt is treated with alcohol, a syrupy precipitate is formed which decomposes into the potassium salt and ammonia when washed with alcohol. It is therefore thought to be **ammonium potassium monamidophosphate.**

H. N. Stokes prepared **silver hydromonamidophosphate,** $(NH_2)PO(OH)(OAg)$, by treating a soln. of the potassium salt, feebly acidified with nitric acid, with silver nitrate; or by adding alcohol to a cold soln. of the normal salt in dil. nitric acid. The crystalline powder consists of small needles, or short, thick, hexagonal prisms. The crystals are stable in light; sparingly soluble in water; readily soluble in dil. nitric or acetic acid, or in aq. ammonia. The boiling aq. soln. forms silver phosphate. When the salt is heated, ammonia is given off, and a fusible glass of silver hexametaphosphate is formed. Microscopic plates of **silver monamidophosphate,** $(NH_2)PO(OAg)_2$, are formed when silver nitrate and then ammonia are added to the filtrate from the preceding salt; or a soln. of that salt in dil. nitric acid is treated with silver nitrate and ammonia. The colourless salt is stable in air; it is almost insoluble in water; and soluble in nitric acid, and aq. ammonia. Alcohol precipitates the acid salt from the soln. in dil. nitric acid, and the spontaneous evaporation of the ammoniacal soln. furnishes the unchanged salt. The anhydrous salt is not changed at 150°, but at 180° it gives off half the nitrogen as ammonia, and forms an imidopyrophosphate, $NH\{PO(OAg)_2\}_2$; it is possible that H. Schiff obtained **lead monamidophosphate,** as a voluminous, white precipitate, insoluble in ammonia, by adding lead acetate to a soln. of the alkali salt. The precipitate is insoluble in ammonia. H. N. Stokes also obtained what was possibly **lead hydromonamidophosphate,** by adding lead acetate to a soln. of the potassium salt. The crystalline precipitate is somewhat soluble in water. He also obtained a **chromium amidophosphate.**

H. N. Stokes prepared **diamidophosphoric acid,** $(NH_2)_2PO(OH)$, by treating phenyl dichlorophosphate, $Cl_2.PO.OC_6H_5$, with ammonia to convert it into phenyldiamidophosphate, $(NH_2)_2PO.OC_6H_5$, and hydrolyzing the product with a soln. of potassium diamidophosphate. When a cold soln. of this salt is treated with acetic acid, crystals of diamidophosphoric acid are formed. If silver diamidophosphate is treated with hydrogen sulphide, the clear filtrate contains a soln. of the acid, which can be precipitated with alcohol. The salt can be purified by dissolving it in water, and again precipitating the aq. soln. with alcohol. This acid has been also called *phosphodiamic acid* or *phosphodiamidic acid.* The microscopic crystals consist of six-sided plates which are stable in air; freely soluble in water; almost insoluble in alcohol; easily decomposed by acids; and scarcely attacked by boiling alkali-lye. Cold nitric acid transforms diamidophosphoric acid into monamidophosphoric acid, and finally into ordinary phosphoric acid, but there are no signs of any differences in the nature of the two amido-groups. The diamidophosphates of the alkalies and alkaline earths are very soluble in water and have not been obtained in a crystalline state pure enough for analysis. A mol of the free acid unites with a mol of ammonia to form **ammonium diamidophosphate**; but with 2 mols of ammonia the soln. possesses the smell of that gas, and gives with silver nitrate a mixture of the primary and secondary silver salts. Soln. of the alkali hydroxide and the acid furnish non-crystallizable **potassium and sodium diamidophosphates,** which are readily soluble in water. By adding the calculated quantity of silver nitrate to a dil. soln. of the barium salt; washing the white, pulverulent precipitate; dissolving it in aq. ammonia; and re-precipitating with dil. nitric acid, white, pulverulent **silver diamidophosphate,** $(NH_2)_2PO(OAg)$, is formed. This salt can be obtained in short rhombohedral prisms by the slow evaporation of the ammoniacal soln. over sulphuric acid. The salt is almost insoluble in water, but freely soluble in ammonia. The ammoniacal soln. furnishes imidoamidophosphate when treated with silver nitrate. No ammonia is given off by the salt when confined over sulphuric acid, or when heated to 100°. The salt loses weight slowly when heated to 150°–160°; and when rapidly heated to a higher temp., the salt swells up, develops ammonia, and melts to a grey mass. For the action of potassium hydroxide, *vide supra,* trihydroxydiamidophosphoric acid.

H. Schiff claimed to have prepared $PO(NH_2)_3$, or **phosphoryl triamide,** by slowly leading a current of dry ammonia into cold phosphoryl chloride until the mass was quite sat. The ammonium chloride was washed from the product of the action with cold or warm water, and phosphoric triamide remained as a snow-white powder. H. Schiff claimed that the compound is scarcely attacked by boiling water, an aq. soln. of potassium hydroxide, or dil. acids; but that it is slowly attacked by conc. acids. When fused with potassium hydroxide, ammonium and potassium phosphates are formed; and when heated out of contact with air, ammonia, and phosphoryl nitrile are produced: $PO(NH_2)_3=PON+2NH_3$. J. H. Gladstone, A. Mente, and H. N. Stokes failed to confirm the preparation of H. Schiff's *triphosphoramide.* According to J. H. Gladstone, the third atom of chlorine cannot be replaced by an amido-group at any temp. below that at which further decomposition occurs (300°). The product of the action of ammonia on phosphoryl chloride is a mixture of ammonium salts of amido- and imido-tetraphosphoric acids.

C. Poulenc reported **phosphorus diamidotrifluoride,** $PF_3(NH_2)_2$, to be formed by the action of ammonia on phosphorus trifiuodichloride: $PF_3Cl_2+4NH_3=2NH_4Cl+PF_3(NH_2)_2$, as a white mass which cannot be separated from the ammonium chloride. When heated it furnishes phospham. T. E. Thorpe and J. W. Rodger obtained **thiophosphoryl diamidofluoride,** $PS(NH_2)_2F$, by the action of ammonia on thiophosphoryl fluoride: $PSF_3+4NH_3=2NH_4F+PS(NH_2)_2F$. The white mass deliquesces in air, and when treated with water furnishes diamidophosphoric acid: $PS(NH_2)_2F+H_2O=HF+PS(NH_2)_2OH$; and with a soln. of cupric sulphate it gives a yellowish precipitate which rapidly darkens, forming cupric sulphide; the filtrate, on standing, yields bluish-green crystals of $Cu_3(PO_4)_2.CuSiF_6$. J. H. Gladstone and J. D. Holmes had previously obtained **thiophosphoryl diamidochloride,** $PS(NH_2)_2ClS$, by the action of ammonia on thiophosphoryl chloride, and found that with water it yields diamidothiophosphoric acid. H. Schiff represented the reaction with ammonia in a different way: $PSCl_3+6NH_3=3NH_4Cl+PS(NH_2)_3$.

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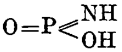
[2] H. N. Stokes, *Amer. Chem. Journ.*, **15**. 198, 1893; **16**. 123, 140, 1894; **20**. 740, 1898; *Zeit. anorg. Chem.*, **19**. 42, 1899; A. Sabanéeff, *ib.*, **17**. 486, 1898; *Journ. Russ. Phys. Chem. Soc.*, **30**. 403, 1898; A. Mente, *Liebig's Ann.*, **248**. 232, 1888; H. Schiff, *ib.*, **101**. 292, 1857; **103**. 168, 1857; *Journ. prakt. Chem.*, (1), **71**. 161, 1857; (1), **72**. 331, 1857; *Zeit. Chem.*, (2), **5**. 609, 1869; J. H. Gladstone, *Journ. Chem. Soc.*, **2**. 121, 1850; **3**. 135, 353, 1851; **22**. 15, 1869; J. H. Gladstone and J. D. Holmes, *ib.*, **18**. 7, 1865; T. E. Thorpe and J. W. Rodger, *ib.*, **55**. 318, 1889; *Chem. News*, **59**, 236, 1889; C. Poulenc, *Compt. Rend.*, **113**. 75, 1891; *Ann. Chim. Phys.*, (6), **24**. 584, 1891.

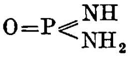
§ 67. Derivatives of Imidophosphoric Acid

By abstracting the elements of ammonia from the di- and tri-amidophosphoric acids, a series of **imido-compounds** has been prepared; these are represented by:



$O=P<^{NH}_{OH}$

Imidophosphoric acid.



$O=P<^{NH}_{NH_2}$

Phosphoryl imidoamide.

$O=P\equiv N$

Phosphoryl nitrile.

According to H. Schiff,[1] ammonia reacts with phosphorus pentoxide, forming what he called *Phosphaminsäure*, and his analyses agree with his empirical formula, PO.NH.OH—not $PO(NH_2)(OH)_2$. According to H. N. Stokes, the product of the reaction is a mixture consisting largely of this acid, which he called **imidophosphoric acid,** PO.NH.OH, or, perhaps, HO.PO : NH. The mixture is readily soluble in water and alcohol. It is not easily oxidized to phosphoric acid; ammonia is evolved when the mixture is boiled with water. The acid forms a series of salts which have not been obtained pure; the soluble salts give precipitates with the salts of the heavy metals—*e.g.* the precipitates with zinc, cadmium, lead, silver, and tin salts are white; with copper and nickel salts, blue; and with cobalt salts, violet. The precipitates are soluble in soln. of ammonia, and ammonium chloride and in acids. J. H. Gladstone and J. D. Holmes emphasized the general resemblance between the properties of H. Schiff's acid and what they called *pyrophosphodiamic acid*—*i.e. diamidodiphosphoric acid*—and they considered H. Schiff's acid to be a mixture of the latter with metaphosphoric acid. According to A. Mente, the product of the reaction between ammonia and phosphorus pentoxide below 0°, is imidodiphosphoric acid, and A. Mente considers that J. H. Gladstone and J. D. Holmes' diamidodiphosphoric acid and his imidodiphosphoric acid are the same.

Ammonia is absorbed by the phosphorus tri- and penta-chlorides with the evolution of much heat. According to A. Besson, ammonia unites directly with phosphorus pentachloride (dissolved in carbon tetrachloride) to form a white addition product, $PCl_5.8NH_3$; and, according to H. Rose, with phosphorus trichloride, to form the addition compound, $PCl_3.5NH_3$. At ordinary temp., some complicated reactions occur. Thus, (i) according to H. Rose, if the product of the action be extracted with ether, nitrogen phosphochloride, $N_3P_3Cl_6$, is obtained; (ii) according to C. Gerhardt, if the product be heated, hydrogen chloride and ammonium chloride are evolved, and a white powder called *phospham*, $(PN_2H)_n$, is obtained (*q.v.*); and (iii) according to C. Gerhardt, if the product be thoroughly washed, a white powder called **phosphamide,** or **phosphoryl imidoamide,** $[(NH_2)PO(NH)]_n$, remains. Phosphoryl imidoamide was obtained by C. Gerhardt by saturating phosphorus pentachloride with ammonia; extracting the white product with water to remove ammonium chloride; then boiling with a dil. soln. of alkali carbonate or hydroxide; then with dil. nitric or sulphuric acid; then with water; and finally heating so as to sublime any remaining ammonium chloride. F. Wöhler and J. von Liebig had previously noted how difficult it is to remove the soluble chloride from the product of the action of ammonia on phosphorus pentachloride. J. H. Gladstone extracted the mass with ether, or by a prolonged boiling in water. The mol. wt. of phosphoryl imidoamide is unknown, but it is generally thought to be higher than that represented by the regular formula, $NH_3.PO.NH$. The white powder is insoluble in the usual solvents, but is slowly transformed into phosphoric acid and ammonia when boiled with water. When heated out of contact with air, it forms ammonia and phosphoryl nitrile; when heated in moist air it gives metaphosphoric acid and ammonia; when fused with alkali hydroxide it gives ammonia and the alkali phosphate; and when heated with copper, it forms ammonia and silvery copper phosphide along with a reddish substance—possibly cuprous phosphate. Phosphamide resists the action of most oxidizing agents; it is not attacked by chlorine, boiling conc. hydrochloric acid, nitric acid, or aqua regia; nor is it attacked by cold sulphuric acid, but the hot acid forms phosphoric acid: $NH_2.PO.NH+2H_2SO_4+3H_2O=H_3PO_4+2(NH_4)HSO_4$.

When phosphoric imidoamide, phosphortriamide or a chloramide is heated, for preference in an oxygen-free gas, **phosphoryl nitrile,** PNO, is formed: $NH_2.PO:NH=NH_3+PNO$; or $PO(NH_2)_3=2NH_3+PNO$. This compound was described by C. Gerhardt in 1846 as *biphosphamide,* by J. H. Gladstone in 1850 as *phosphonitryle,* and by H. Schiff in 1857 as *monophosphamide.* It is a white powder which melts at a red-heat, and, on cooling, forms a black, glassy mass. It unites neither with alkalies nor acids, nor is it affected by boiling nitric acid. It is oxidized to phosphoric acid when fused with alkalies in air or with oxidizing agents. It forms ammonia when heated with hydrogen, and with steam, it forms an oxide of phosphorus and phosphine. The high m.p., and its inertness towards solvents, have led to the belief that the mol. is more complex than is represented by the simple formula PNO—G. Oddo thinks the mol. is $P_2N_2O_2$, or $NP{<}O_2{>}PN$.

According to A. Besson and G. Rosset, when phosphorus chloronitride is heated with nitrogen peroxide at 200°–250° in a sealed tube, nitrogen, nitrous and nitric oxides, chlorine, nitrosyl, and nitroxyl chlorides, and a substance of the composition $2P_2O_5,NO_2$, **phosphatonitroxyl,** are formed. This substance has been also obtained by heating phosphoric oxide with nitrogen peroxide at 200° in a sealed tube; it gives off nitrogen peroxide when heated, and deliquesces in the air with loss of nitrogen peroxide.

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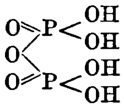
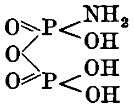
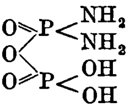
[1] H. Schiff, *Zeit. Chem.*, (2), **5**. 609, 1869; *Journ. prakt. Chem.*, (1), **71**. 161, 1857; (1), **72**. 331, 1857; *Liebig's Ann.*, **101**. 299, 1857; **103**. 168, 1857; A. Mente, *ib.*, **248**. 232, 1888; F. Wöhler and J. von Liebig, *ib.*, **11**. 142, 1834; J. H. Gladstone, *Journ. Chem. Soc.*, **2**. 121, 1850; **3**. 135, 3153, 1851; **22**. 15, 1869; J. H. Gladstone and J. D. Holmes, *ib.*, **17**. 225, 1864; **19**. 1, 1866; **21**. 64, 1868; *Proc. Roy. Soc.*, **15**. 510, 1867; *Chem. News*, 9. 260, 1864; **12**. 282, 1865; H. N. Stokes, *Amer. Chem. Journ.*, **15**. 198, 1893; **16**. 123, 140, 1894; **17**. 275, 1895; **18**. 629, 1896; **20**. 740, 1898; *Zeit. anorg. Chem.*, **19**. 42, 1899; C. Gerhardt, *Ann. Chim. Phys.*, (3), **18**. 188, 1846; (3), **20**. 255, 1847; *Journ. Pharm. Chim.*, (3), **11**. 457, 1847; G. Oddo, *Gazz. Chim. Ital.*, **29**. ii, 330, 1899; H. Rose, *Pogg. Ann.*, **24**. 308, 1832; **28**. 529, 1833; A. Besson, *Compt. Rend.*, **111**. 972, 1891; **14**. 1264, 1892; A. Besson and G. Rosset, *ib.*, **143**. 37, 1906.

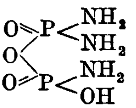
§ 68. The Amidodiphosphoric or Amidopyrophosphoric Acids

The chemistry of the amido- and imido-diphosphoric acids is not in a satisfactory state. The interpretation of the experimental work by different investigators is discordant, showing a lack of precise facts. The reports of the preparation and properties of the three amidophosphoric acids indicated above are largely based upon the work of J. H. Gladstone and J. D. Holmes.[1] A. Mente's and H. N. Stokes' re-survey of the field outlined by J. H. Gladstone and J. D. Holmes shows that the interpretation of the results was probably erroneous; in othe words, the amido-diphosphoric acids reported by J. H. Gladstone and J. D. Holmes may really be imido-diphosphoric acids, or mixtures of the same with meta- and pyro-phosphoric acids. A number of amidopyrophosphoric acids have been reported. For instance, starting from di- or pyro-phosphoric acid, $O[PO(OH)_2]_2$, and replacing the HO-groups by NH_2-groups, one by one,


Diphosphoric acid.


Monamidodiphosphoric acid.


Diamidodiphosphoric acid.


Triamidodiphosphoric acid.

J. H. Gladstone and J. D. Holmes claimed to have made the tribasic **monamidodiphosphoric acid,** $(NH_2)P_2O_3(OH)_3$—which they called *diphosphamidic acid*—or its salts by the hydrolysis of an aq. soln. of nitrilodiphosphoric acid: $(NH_4O)P_2O_3{\vdots}N+2H_2O=NH_3+(NH_2)P_2O_3(OH)_3$; by the hydrolysis of an aq. soln. of diamidodiphosphoric acid, or of its salts: $(NH_2)_2P_2O_3(OH)_2+H_2O=NH_3+(NH_2)P_2O_3(OH)_3$; by heating the diamidodiphosphoric acid or its salts with an acidified soln. of a metal salt, $(NH_2)_2P_2O_3(OK)_2+KCl+H_2O=(NH_2)P_2O_3(OK)_3+NH_4Cl$; or by saturating an aq. soln. of pyrophosphoric acid with ammonia, and adding baryta-water—not in excess. As a result, ammonia is evolved, and barium monamidodiphosphate is precipitated. The salts in question are not very soluble in acids; they give a characteristic red coloration with ferric chloride. According to H. N. Stokes, monamidodiphosphoric acid is thought to be identical with A. Mente's imidodiphosphoric acid, $\{PO(OH)_2\}_2NH$, or $\{PO(OH).O.PO(OH)\}NH$. For **ammonium monamidodiphosphate,** *vide infra,* the diamidotetraphosphates. J. H. Gladstone treated the salt with potassium hydroxide, and obtained a gummy mass containing **potassium monamidodiphosphoric acid** when the neutral soln. was evaporated over sulphuric acid. The composition was variable owing to the decomposition of the unstable salt. If the neutral ammonium salt obtained by the action of alcoholic ammonia on phosphorus chloronitride be treated with an excess of silver nitrate, and the filtrate boiled, the **silver monamidodiphosphate,** $(NH_2)P_2O_3(OAg)_3$, is deposited as a white precipitate; again, if the ferric salt be treated with a cold soln. of potassium hydroxide, and the neutral liquid treated with silver nitrate, the same salt is formed. J. H. Gladstone made **barium monamidodiphosphate,** $(NH_2.P_2O_3.O_2)Ba$, by neutralizing an aq. soln. of pyrophosphoric acid with ammonia, and adding the calculated quantity of baryta-water. J. H. Gladstone and J. D. Holmes made it by dissolving phosphorus chloronitride in alcoholic ammonia and mixing the soln. with an excess of barium chloride. The filtrate when boiled deposits first barium diamidodiphosphate which when boiled still more passes into the monamido-salt. It is soluble in nitric and hydrochloric acids, and insoluble in acetic acid. J. H. Gladstone also made the **copper, silver, barium, lead, tin, chromium, manganese, ferric, cobalt, nickel, and platinum monamidodiphosphates.** The iron salt furnishes an ammino-salt. No **antimony or gold monamidodiphosphate** could be obtained.

The *tetramidodiphosphoric acid,* $(NH_2)_2PO.O.PO(NH_2)_2$, has not been reported. J. H. Gladstone and J. D. Holmes prepared dibasic **diamidodiphosphoric acid,** $(NH_2)_2P_2O_3(OH)_2$, or, as they called it, *diphosphodiamidic acid,* by the hydrolysis of nitrogen chlorophosphide, $N_3P_3Cl_6$, with alcoholic potash-lye, and afterwards with water: $2N_3P_3Cl_6+15H_2O=12HCl+3(NH_2)_2P_2O_3(OH)_2$; by the hydrolysis of aq. soln. of mono- or di-amidophosphorus oxychlorides, *i.e.* the product obtained by saturating phosphoryl chloride at a low temp. with ammonia, or by dropping phosphoryl chloride into conc. aq. ammonia: $2POCl_3+2NH_3+3H_2O=6HCl+(NH_2)_2P_2O_3(OH)_2$; or by the action of phosphorus pentachloride on conc., well-cooled, aq. ammonia. The hydrolysis of the higher amidophosphoric acids or imidoamidophosphoric acid can be symbolized: $2(NH_2)PONH+H_2SO_4+3H_2O=(NH_4)_2SO_4+(NH_2)_2P_2O_3(OH)_2$. According to H. Schiff, diamidodiphosphoric acid can be prepared by the action of ammonia gas on phosphoric pentoxide: $P_2O_5+2NH_3=(NH_2)_2P_2O_3(OH)_2$. While H. Schiff thought that the product of this last reaction was imidophosphoric acid, (NH)PO(OH), J. H. Gladstone and J. D. Holmes considered it to be diamidodiphosphoric acid; and A. Mente thought that the product of the reaction is a mixture of potassium meta- and pyrophosphates with the potassium salt of diimidophosphoric acid, $NH(PO)_2NH(OH)_2$. The acid is said to decompose into phosphorus pentoxide and ammonia when it is heated; the normal salts have been described. The insoluble metal salts dissolve in a soln. of ammonium chloride; and they are not so soluble in acids as the orthophosphates. Ammonia is formed when the salts are fused with potassium hydroxide, and they are but slowly oxidized to normal phosphates by treatment with a mixture of nitric acid and potassium chlorate. A. Mente thinks that this acid is identical with imidodiphosphoric acid. According to J. H. Gladstone and J D. Holmes, the acid is a colourless mass which readily dissolves in alcohol and in water. It decomposes into phosphorus pentoxide and ammonia when heated; and when its aq. soln. is boiled, or when its salts are treated with an excess of a metal salt soln., it forms ammonia and monamidodiphosphoric acid. If the soln. strongly acidified with sulphuric acid be treated with ferric chloride, until the soln. is red, and then boiled, the liquid becomes turbid, and a gelatinous precipitate of a ferric salt is formed which, when heated, gives off ammonia, without melting.

The acid is dibasic, and only the normal salts are known with certainty. The insoluble metal salts dissolve in soln. of ammonium chloride, and in dil. acids; they give off ammonia when fused with potassium hydroxide; and when evaporated many times with a mixture of nitric acid and potassium chlorate, the salts are transformed into orthophosphates. The modes of preparation of diamidophosphoric acid in ammoniacal soln., and the treatment of the acid with ammonia, furnishes a soln. of **ammonium diamidodiphosphate,** $(NH_2)_2P_2O_3(ONH_4)_2$, which yields radiating masses of crystals. H. Schiff said that during the evaporation there is always some ammonium phosphate formed which contaminates the final product. J. H. Gladstone and J. D. Holmes said that the ammonium salt is produced by burning phosphorus under a bell-jar standing over conc. aq. ammonia. They were not able to prepare **potassium diamidodiphosphate. Copper diamidodiphosphate** was also prepared. If the soln. obtained by treating phosphorus chloronitride with alcoholic ammonia be neutralized and mixed with silver nitrate, a mixture of silver chloride and **silver diamidodiphosphate,** $(NH_2)_2P_2O_3(OAg)_2$, is precipitated. Hot dil. nitric acid extracts the latter salt. J. H. Gladstone and J. D. Holmes made **barium diamidodiphosphate,** $(NH_2)_2P_2O_3(O_2Ba)$, as indicated in connection with the monamidodiphosphate. H. Schiff also prepared this salt. He also obtained strontium and calcium diamidodiphosphates; no **magnesium, mercuric, ferric, chromium, aluminium, or antimony diamidodiphosphate** was prepared, but **zinc, cadmium, manganese, cobalt, and nickel diamidodiphosphates** were obtained.

J. H. Gladstone and J. D. Holmes prepared monobasic **triamidodiphosphoric acid,** $(NH_2)_3P_2O_3(OH)$—also called *diphosphotriamidic acid*—by heating to 230° the product obtained by saturating phosphoryl chloride with ammonia, and then boiling it for a short time with water: $2POCl_3+3NH_3+2H_2O=(NH_2)_3P_2O_3(OH)+6HCl$. The acid is a white, tasteless powder; its aq. soln. reddens litmus, and expels carbon dioxide from carbonates. When heated, it decomposes into ammonia and ammonium nitrilopyrophosphate. When boiled with water, it forms diamidodiphosphoric acid and ammonia; with boiling hydrochloric acid it forms phosphoric acid and ammonium chloride; and with conc. sulphuric acid, ammonium diamidodiphosphate and sulphate. Triamidodiphosphoric acid forms a series of salts. The salts—even the alkali salts—are but sparingly soluble in water. J. H. Gladstone and J. D. Holmes report that it forms salts corresponding with the monobasicity of the acid; and also salts containing up to four atoms of the metal per mol of acid. Hence J. H. Gladstone and J. D. Holmes postulated a tetrabasic *triimidodiphosphoric acid*—possibly $(NH)_3P_2(OH)_4$. The alkali salts are insoluble in water and in acids. The acid reacts with metal salt soln. and metal oxides, forming insoluble salts. According to A. Mente, this acid is identical with diimidodiphosphamidic acid, $(NH)_2P_2O_2(NH_2)OH$. When the acid is treated with ammonium carbonate, **ammonium triamidodiphosphate,** $(NH_2)_3P_2O_3(ONH_4)$, is formed as an insoluble, white mass. A similar product, **potassium triamidodiphosphate,** is obtained by the action of potassium carbonate on the acid. According to J. H. Gladstone, he obtained mono- and di- **copper triamidodiphosphates** ; and he prepared **silver triamidodiphosphate,** $(NH_2)_3P_2O_3(OAg)$, as an amorphous, white, flocculent precipitate, by adding a soln. of silver nitrate to the acid suspended in cold water. The salt is insoluble in water. Dil. nitric acid, or aq. ammonia, extracts some silver from the salt, and hydrochloric acid decomposes it completely. J. H. Gladstone also obtained orange-yellow **trisilver triamidodiphosphate,** $(NH_2)(NHAg)_2P_2O_3(OAg)$, by adding a soln. of the acid to a feebly ammoniacal soln. of silver oxide ; or by treating the monosilver salt with an ammoniacal soln. of a silver salt. The precipitate is washed by decantation. Dil. aq. ammonia, or dil. nitric acid, transforms it into the monosilver salt ; boiling acetic acid acts similarly, but more feebly. J. H. Gladstone made **barium triamidodiphosphates,** $(NH_2)_2(NH.Ba:O)P_2O_3$, by adding barium chloride to the acid suspended in aq. ammonia, and also $\{(NH_2)_3P_2O_3\}_2Ba$, by suspending the acid in a soln. of barium chloride, and neutralizing the hydrochloric acid which is formed by means of ammonia. If the acid mixed with water is treated with an ammoniacal soln. of a magnesium salt, and the precipitate washed with water, J. H. Gladstone obtained a mixture of the **magnesium triamidodiphosphate,** $(NH_2)_2(NH.Mg.O)P_2O_3$, and $MgH_2(P_2O_4N_3)_2$. He also made the **mercury, lead, iron, cobalt, and platinum triamidodiphosphates.**

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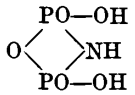
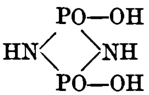
[1] H. Schiff, *Zeit. Chem.*, (2), **5**. 609, 1869 ; *Journ. prakt. Chem.*, (1), **71**. 161, 1857 ; (1), **72**. 331, 1857 ; *Liebig's Ann.*, **101**. 299, 1857 ; **103**. 168, 1857 ; A. Mente, *ib.*, **248**. 232, 1888 ; J. H. Gladstone, *Journ. Chem. Soc.*, **2**. 121, 1850 ; **3**. 135, 3153, 1851 ; **22**. 15, 1869 ; J. H. Gladstone and J. D. Holmes, *ib.*, **17**. 225, 1864 ; **19**. 1, 1866 ; **21**. 64, 1868 ; *Proc. Chem. Soc.*, **15**. 510, 1867 ; *Chem. News*, **9**. 260, 1864 ; **12**. 282, 1865 ; H. N. Stokes, *Amer. Chem. Journ.*, **15**. 198, 1893 ; **16**. 123, 140, 1894 ; **17**. 275, 1895 ; **18**. 629, 1896 ; **20**. 740, 1898 ; *Zeit. anorg. Chem.*, **19**. 42, 1899.

§ 69. Imidodiphosphoric or Imidopyrophosphoric Acid

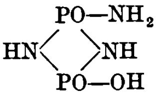
By the loss of the elements of water or ammonia from imidodiphosphoric acid there is formed diimidodiphosphoric acid, or mixed imido-amido-diphosphoric acids also called imido-diphosphamic or imido-diphosphamidic acid :



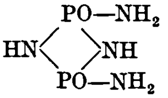
Imidodiphosphoric acid.



Diimidodiphosphoric acid.

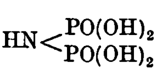


Diimidomonamidodiphosphoric acid.



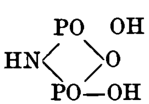
Diimidodiamidodiphosphoric acid.

According to H. N. Stokes, and A. Mente, there are two **monimidodiphosphoric acids,** differently constituted, but not isomeric—one is dibasic, and the other tetrabasic. H. N. Stokes[1] prepared the **tetrabasic monimidodiphosphoric acid**



$$HN{<}\begin{matrix}PO(OH)_2\\PO(OH)_2\end{matrix}$$

Tetrabasic monimidodiphosphoric acid, $NH[PO(OH)_2]_2$.



Dibasic monimidodiphosphoric acid, $PO(OH).O.PO(OH)NH$.

by heating trimetaphosphimic acid, $P_3N_3O_6H_6$ (*vide infra*), for about seven minutes ; on treating the ammoniacal soln. with a magnesium salt, magnesium ortho- and pyro-phosphates are precipitated, and the soluble magnesium imidodiphosphate remains in soln. By the addition of silver nitrate to this soln. a colourless, crystalline precipitate, sparingly soluble, trisilver hydroimidodiphosphate, $NHP_2O_2(OAg)_3OH$, is formed. The imidodiphosphate can be separated from the other phosphates by the treatment of their sodium salts with alcohol. The free acid has not been obtained. The acid is fairly stable in cold soln., but gradually decomposes into trimetaphosphimic acid. According to H. N. Stokes, the acid is probably identical with the so-called monamidodiphosphoric acid. The acid (or rather its salts) cannot be referred to the formula $(HO)_2PO.O.PO(NH_2)OH$, because the formation of pyrophosphate and not of orthophosphate would be expected, whereas if the constitution be $HN[PO(OH)_2]_2$, only orthophosphoric acid would be formed. Hence, it is possible that the constitution may be $(HO)_2PO.O.PO(NH_2)OH$.

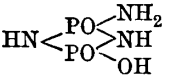
According to H. N. Stokes, **trisodium imidodiphosphate,** $NHP_2O_2(ONa)_3(OH)$, is produced when the trisilver salt is treated with sodium chloride. On evaporating the clear soln., a gummy mass is obtained; and the aq. soln. when treated with alcohol furnishes a non-crystallizable syrup. The salt is more soluble in dil. alcohol than sodium pyrophosphate. The **trisilver imidodiphosphate,** $NHP_2O_2(OAg)_3(OH)$, is formed by precipitation from the free acid or a tribasic salt soln. by silver nitrate. The white amorphous precipitate is insoluble in water, and stable in light. There are two modifications of **tetrasilver imidodiphosphate,** $NHP_2O_2(OAg)_4$—one is white, the other yellow. H. N. Stokes suggested that they are tautomeric modifications. The white form is obtained by adding sodium imidodiphosphate to a soln. of silver oxide in ammonium nitrate. The voluminous precipitate is stable only in the presence of its mother-liquor. It readily passes into the yellow form—*e.g.* by boiling the white form in its mother-liquor. The yellow form is amorphous. The amorphous precipitate is obtained by adding an excess of silver nitrate to an ammoniacal soln. of an imidodiphosphate. H. N. Stokes obtained **magnesium imidodiphosphate** as an amorphous, voluminous precipitate, almost insoluble in water, and freely soluble in soln. of ammonium salts.

According to A. Mente, a **dibasic imidodiphosphoric acid** is formed when a soln. of (4 grms.) ammonium carbonate, $(NH_2)CO(ONH_4)$, in (10 grms.) phosphoryl chloride is warmed to about 50° for a few hours. The reaction is supposed to occur in two stages: $4POCl_3+3(NH_4O)CO(NH_2)=2NH(POCl_2)_2+3CO_2+4NH_4Cl$; followed by $3H_2O+NH(POCl_2)_2=NH(PO.OH)_2O+4HCl$. The acid soln. is treated with ferric or barium chloride in order to precipitate the sparingly soluble ferric or barium salt. It is also formed by boiling diimidodiphosphoric acid with an acid soln. of ferric chloride so as to furnish the ferric imidodiphosphate which forms a good starting-point for the preparation of the other salts. The probable constitution is deduced from the mode of formation. This acid may be identical with the so-called amidodiphosphoric acid. The acid is dibasic, and the existence of a basic salt is in harmony with the assumption that an imido-group is present. A direct determination of the water in the imidophosphate is not possible; if the salt dried to constant weight over sulphuric acid be heated to 100°–110°, there is first a small decrease in weight followed by an increase which was not observed to attain a constant value. A. Mente prepared **barium imidodiphosphate,** $NHP_2O_5Ba.H_2O$, as a voluminous precipitate, by adding barium chloride to an ammoniacal soln. of the acid, or of the ammonium salt.

A. Mente prepared **diimidodiphosphoric acid,** $NH(PO)_2NH(OH)_2$, by heating a soln. containing an excess of ammonium carbamate in phosphoryl chloride, or better in a soln. of phosphoryl chloride in benzene. The reaction is supposed to occur in two stages: $2POCl_3+3(NH_4O)CO(NH_2)=4NH_4Cl+3CO_2+NH(PO)_2NH(Cl_2)$; followed by $NH(PO)_2NH(Cl_2)+2H_2O=2HCl+NH(PO)_2NH(OH)_2$. The dibasic acid has not been isolated. The aq. soln. reacts acid. A hydrogen atom of each of the imido-groups can also be displaced by an equivalent metal. See diamidodiphosphoric acid for other modes of preparation and properties, for the two acids are probably the same. A. Mente prepared **barium diimidodiphosphate,**

$NH(PO)_2NH(O_2Ba)$, by adding barium chloride to a soln. of the acid neutralized with ammonia. It is also formed when diimidomonamidophosphoric acid is boiled with baryta-water, or an ammoniacal soln. of barium chloride. It is sparingly soluble in dil. acids; and loses no water at 100°.

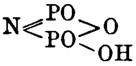
A. Mente prepared monobasic **diimidomonamidophosphoric acid,** or *diimidodiphosphorylmonoaminic acid,* $NH(PO)_2NH(OH)(NH_2)$,



$$\mathrm{HN}<\begin{matrix}\mathrm{PO}<\mathrm{NH_2}\\ >\mathrm{NH}\\ \mathrm{PO}<\mathrm{OH}\end{matrix}$$

by saturating phosphoryl chloride with ammonia, and washing the white mass with water. He supposed the reaction takes place in two stages: $2POCl_3 + 8NH_3 = 5NH_4Cl + NH(PO)_2NH(Cl)NH_2$, followed by the hydrolysis of the monochloride to hydrochloric acid and diimidomonamidophosphoric acid or *diimidodiphosphoamidic acid.* By boiling the acid with soda-lye, one-third of the total nitrogen is evolved as ammonia, and a salt of diimidodiphosphamidic acid is formed. The free acid reddens litmus. See triamidodiphosphoric acid for other modes of preparation and properties, for the two acids are probably the same.

According to J. H. Gladstone and J. D. Holmes, when potassium triamidodiphosphate is heated, it loses the equivalent of two mols of ammonia, and forms **potassium nitrilodiphosphate,** $(KO)P_2O_3N$, corresponding with **nitrilodiphosphoric acid,**



$$\mathrm{N}\lessdot\begin{matrix}\mathrm{PO}\\ \mathrm{PO}\end{matrix}\begin{matrix}>\mathrm{O}\\ <\mathrm{OH}\end{matrix}$$

The potassium salt is but sparingly soluble in water, and when suspended in dil. nitric acid, and treated with silver nitrate, it forms **silver nitrilodiphosphate,** $N:P_2O_3(OAg)$. The **ammonium nitrilodiphosphate,** $N:P_2O_3(ONH_4)$, is formed by heating triamidodiphosphoric acid. The ammonium salt is insoluble in water, but it is slowly hydrolyzed by water, forming ammonia and monamidodiphosphoric acid along with a trace of tetramidotetraphosphoric acid. The free acid has not been prepared.

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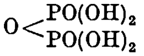
[1] H. N. Stokes, *Amer. Chem. Soc.*, **15.** 198, 1893; **16.** 123, 140, 1894; **20.** 740, 1898; *Zeit. anorg. Chem.*, **19.** 42, 1899; A. Mente, *Liebig's Ann.*, **248.** 232, 1888; J. H. Gladstone and J. D. Holmes, *Journ. Chem. Soc.*, **17.** 225, 1864; **19.** 1, 1866; **21.** 64, 1868; *Proc. Roy. Soc.*, **15.** 510, 1867; *Chem. News*, **9.** 260, 1864; **12.** 282, 1865.

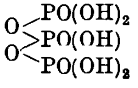
§ 70. Amides and Imides of the Higher Phosphoric Acids

Amido- or imido- derivatives of still higher phosphoric acids have been reported, principally by H. N. Stokes.[1]



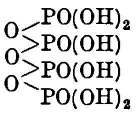
$$\mathrm{O}<\begin{matrix}\mathrm{PO(OH)_2}\\ \mathrm{PO(OH)_2}\end{matrix}$$

Diphosphoric acid.



$$\begin{matrix}\mathrm{O}<\mathrm{PO(OH)_2}\\ >\mathrm{PO(OH)}\\ \mathrm{O}<\mathrm{PO(OH)_2}\end{matrix}$$

Triphosphoric acid.

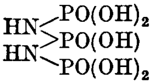


$$\begin{matrix}\mathrm{O}<\mathrm{PO(OH)_2}\\ >\mathrm{PO(OH)}\\ \mathrm{O}\\ >\mathrm{PO(OH)}\\ \mathrm{O}<\mathrm{PO(OH)_2}\end{matrix}$$

Tetraphosphoric acid.

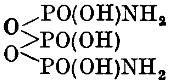
H. N. Stokes prepared **diimidotriphosphoric acid,** $PO(OH)_2.NH.PO(OH).NH.PO(OH)_2$, by heating trimetaphosphimic acid for about seven minutes with nitric acid. The soln. was then treated with an excess of ammonia, and a magnesium salt, and filtered. The acid in question appeared in the filtrate. The silver salt was precipitated by the addition of silver nitrate. Diimidotriphosphoric acid forms two series of salts—an acid salt with three, and a normal salt with five atoms of hydrogen replaced by the metal. For example, **trisodium diimidotriphosphate,**

$P_3N_2O_3H_4Na_3$, forms obtuse prismatic crystals, neutral to litmus, while **pentasodium diimidotriphosphate** has an alkaline reaction. The trisilver salt forms monoclinic crystals. Warming the pentasilver salt with ammonium nitrate destroys the yellow colour—yellow silver phosphate is not whitened by this treatment, while silver trimetaphosphimate becomes orange-yellow. The empirical composition of the acid corresponds with either:



$$\begin{array}{l}\mathrm{HN}{\diagup}\mathrm{PO(OH)_2}\\ \mathrm{HN}{>}\mathrm{PO(OH)}\\ \quad{\diagdown}\mathrm{PO(OH)_2}\end{array}$$

Diimidotriphosphoric acid.

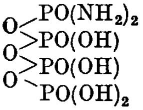


$$\begin{array}{l}\mathrm{O}{\diagup}\mathrm{PO(OH)NH_2}\\ \mathrm{O}{>}\mathrm{PO(OH)}\\ \quad{\diagdown}\mathrm{PO(OH)NH_2}\end{array}$$

Diamidotriphosphoric acid.

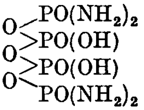
The latter does not agree so well with the existence and properties of the pentasilver salt as the former.

H. N. Stokes has obtained a number of derivatives of tetraphosphoric acid whose empirical compositions agree with the graphic formulæ:



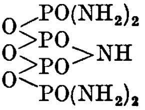
$$\begin{array}{l}\mathrm{O}{\diagup}\mathrm{PO(NH_2)_2}\\ \mathrm{O}{>}\mathrm{PO(OH)}\\ \mathrm{O}{>}\mathrm{PO(OH)}\\ \quad{\diagdown}\mathrm{PO(OH)_2}\end{array}$$

Diamidotetraphosphoric acid.



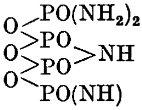
$$\begin{array}{l}\mathrm{O}{\diagup}\mathrm{PO(NH_2)_2}\\ \mathrm{O}{>}\mathrm{PO(OH)}\\ \mathrm{O}{>}\mathrm{PO(OH)}\\ \quad{\diagdown}\mathrm{PO(NH_2)_2}\end{array}$$

Tetramidotetraphosphoric acid.



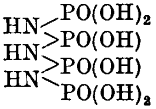
$$\begin{array}{l}\mathrm{O}{\diagup}\mathrm{PO(NH_2)_2}\\ \mathrm{O}{>}\mathrm{PO}{\diagdown}\\ \mathrm{O}{>}\mathrm{PO}{\diagup}{>}\mathrm{NH}\\ \quad{\diagdown}\mathrm{PO(NH_2)_2}\end{array}$$

Monimidotetramidotetraphosphoric acid.



$$\begin{array}{l}\mathrm{O}{\diagup}\mathrm{PO(NH_2)_2}\\ \mathrm{O}{>}\mathrm{PO}{\diagdown}\\ \mathrm{O}{>}\mathrm{PO}{\diagup}{>}\mathrm{NH}\\ \quad{\diagdown}\mathrm{PO(NH)}\end{array}$$

Diimidodiamidotetraphosphoric acid.



$$\begin{array}{l}\mathrm{HN}{\diagup}\mathrm{PO(OH)_2}\\ \mathrm{HN}{>}\mathrm{PO(OH)}\\ \mathrm{HN}{>}\mathrm{PO(OH)}\\ \quad{\diagdown}\mathrm{PO(OH)_2}\end{array}$$

Triimidotetraphosphoric acid.

These obviously represent but a small fraction of those theoretically possible; nor is there any particular evidence outside that furnished by the analysis and the rules of valency to show how the NH-, NH_2-, and the OH-groups are distributed in the mol. According to J. H. Gladstone, by saturating phosphoryl chloride with ammonia, and heating the product to about 200°, a white residue is obtained which furnishes **monimidotetramidotetraphosphoric acid,** $(NH)P_2O_7(NH_2)_4$, or $PO(NH_2)_2.O.(NH).O.PO.O.PO(NH_2)$, on treatment with water. The acid decomposes slowly when digested with water at ordinary temp., and rapidly when boiled. If the acid be treated with conc. aq. ammonia, a white-mass is obtained, which J. H. Gladstone said is not an ammonium salt. It is regarded as **amminomonoimidotetraphosphoric acid,** $NH_3.(NH)P_2O_7(NH_2)_4$. If monoimidotetramidotetraphosphoric acid be treated with a neutral or slightly acid soln. of silver nitrate, a yellowish-brown precipitate of the **silver diimidodiamidotetraphosphate** is obtained. The free acid, **diimidodiamidotetraphosphoric acid,** $(NH)_2P_2O_7(NH_2)_2$, has not been isolated.

H. N. Stokes prepared salts of **triimidotetraphosphoric acid,** $HN\{PO(OH).NH.PO(OH)_2\}_2$, by the hydrolysis of salts of pentametaphosphimic acid—*e.g.* a hot acetic acid soln. of sodium pentametaphosphate furnishes **sodium triimidotetraphosphate,** $NH\{PO(OH).NH.PO(ONa)_2\}_2$; and the addition of silver nitrate to the soln. furnishes the **silver triimidotetraphosphate,** $HN\{PO(OH).NH.PO(OAg)_2\}_2$. The acid is so unstable that it cannot be made by heating tetrametaphosphimate as might have been anticipated by the formation of diimidotriphosphoric acid by the action of heat on trimetaphosphimic acid.

The aq. soln. of the product of the action of gaseous ammonia on phosphoryl chloride contains a mixture of ammonium diamidodiphosphate and several amidotetraphosphates. The latter can be precipitated by treatment with alcohol. If the product is washed with alcohol, dissolved in water, again precipitated with alcohol, and dried in vacuo over sulphuric acid, **triammonium hydrodiamidotetraphosphate,** $(NH_4O)_3(HO)P_4O_7(NH_2)_2$, is formed. Free **diamidotetraphosphoric acid,** $(NH_2)_2P_4O_7(OH)_4$, is not known. The aq. soln. of the ammonium salt gives precipitates with the salts of many of the metals—silver nitrate, for instance, gives a white flocculent precipitate. The precipitates are probably mixtures of several amidotetraphosphates. The ammonium salt is decomposed into ammonium chloride and phosphoric acid when boiled with hydrochloric acid;

and when heated to 100°, it forms a white mass which smells of nicotine, and is possibly *triammonium amidodiphosphate*, $(NH_2)P_2O_3(ONH_4)_3$. Ammonium diamidotetraphosphate unites with ammonium to form a white mass; cold potash-lye decomposes it with the evolution of ammonia; and if covered with alcohol, and allowed to stand for a year, crystals of the ammonium salt of a new acid are formed. If the tertiary ammonium salt is heated to about 220°, it loses ammonia and forms a residue which is possibly **diammonium dihydrodiamidotetraphosphate,** $(NH_2)_2P_4O_7(OH)_2(ONH_4)_2$. This product is decomposed by water, forming diamidodiphosphoric acid, $(NH_2)_2P_2O_3(OH)_2$, and possibly also tetramidotetraphosphoric acid, $(NH_2)_4P_4O_7(OH)_2$.

J. H. Gladstone prepared **tetramidotetraphosphoric acid,** $(NH_2)_4P_4O_7(OH)_2$, by treating ammonium diamidotetraphosphate with mineral acids, potassium carbonate or hydroxide: $(NH_2)_2P_4O_7(OH)(ONH_4)_3+HCl=NH_4Cl+2H_2O+(NH_2)_4P_4O_7(OH)_2$. It is also produced along with diamido- and triamidodiphosphoric acids by the action of cold conc. nitric acid, or potassium carbonate or hydroxide on triammonium hydrodiamidotetraphosphate: $(NH_2)_2P_4O_7(OH)(ONH_4)_3+KOH=NH_3+3H_2O+(NH_2)_4P_4O_7(OH)(OK)$; and by boiling the same salt with water, $(NH_2)_2P_4O_7(OH)(ONH_4)_3=2H_2O+(NH_2)_4P_4O_7(OH)(ONH_4)$. The last reaction may proceed differently: $(NH_2)_2P_4O_7(OH)(ONH_4)_3+3H_2O=5NH_3+2H_4P_2O_7$. Tetramidotetraphosphoric acid does not appear to be affected by acids. The aq. soln. of tetramidotetraphosphoric acid gives no precipitate with hydrochloroplatinic acid. The acid unites with bases, forming salts; thus, **ammonium hydrotetramidotetraphosphate,** $(NH_2)_4P_4O_7(OH)(ONH_4)$, is obtained by neutralizing the acid with ammonia. The ammonium salt is soluble in water; the salt is precipitated from its aq. soln. by alcohol; and when dried in vacuo loses its ammonia. Similarly, **potassium hydrotetramidophosphate,** $(NH_2)_4P_4O_7(OH)(OK)$, can be prepared.

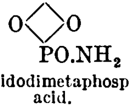
H. N. Stokes also made **sodium amidoheximidoheptaphosphate**—a salt of *amidoheximidoheptaphosphoric acid,* $PO(OH)(NH_2).NH.\{PO(OH)NH\}_5.PO(OH)_2$—by the hydrolysis of heptaphosphoric nitrilochloride with sodium hydroxide in an ethereal soln. He expected to obtain *heptametaphosphimic acid.* The sodium salt is decomposed by acids, forming tetrametaphosphimate.

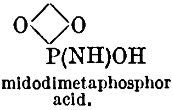
REFERENCES.

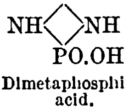
[1] H. N. Stokes, *Amer. Chem. Soc.*, 15. 198, 1893; 16. 140, 1894; 20. 740, 1898; *Zeit. anorg. Chem.*, 19. 42, 1899; J. H. Gladstone, *Journ. Chem. Soc.*, 2. 121, 1850; 3. 135, 353, 1851; 22. 15, 1869.

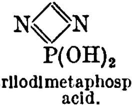
§ 71. The Metaphosphimic Acids and their Salts

Just as the amidophosphoric acids can be called *phosphamic acids* or *phosphamidic acids,* so also can the imidophosphoric acids be called *phosphimic acid* or *phosphimidic acids.* The replacement of two hydroxyl groups or of phosphoryl oxygen in orthophosphoric acid by equivalent bivalent imido- or NH-groups, will furnish *orthophosphimic acids,* HO.PO.NH, or HN: $P(OH)_3$; so also will the substitution of HN-groups in place of the phosphoryl oxygen of metaphosphoric acids, $(HO.PO_2)_n$, furnish a series of polymerized *metaphosphimic acids,* $[HO(NH:P:O)]_n$ or $[PN(OH)_2]_n$. Several isomeric forms of each member of the series are theoretically possible, for example, with the second member, where $n=2$:


Diamidodimetaphosphoric acid.

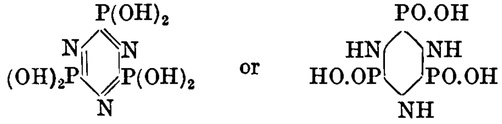

Diimidodimetaphosphoric acid.


Dimetaphosphimic acid.


Nitrilodimetaphosphoric acid.

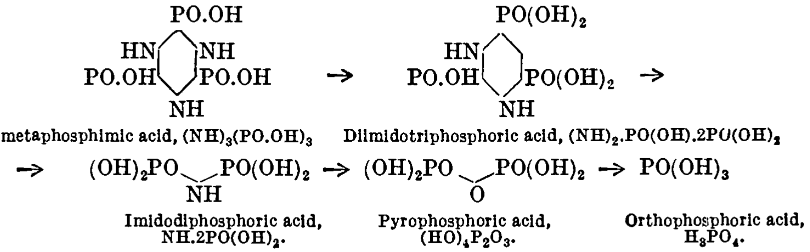
In 1888, A. Mente[1] described a product of the action of ammonium carbamate and water on phosphoryl chloride which he regarded as diimidodiphosphoric acid,

$HN<[PO(OH)]_2>NH$, with a possible constitution analogous with what had just been called *dimetaphosphimic acid*, and which he also considered to be identical with an acid prepared by J. H. Gladstone in 1850, and named *deutazophosphoric acid*, a cognomen subsequently altered to *pyrophosphodiamic acid*, $O[PO(OH)NH_2]_2$, because it was considered to be a diamide of pyrophosphoric acid. H. N. Stokes suggested that J. H. Gladstone's acid was impure **trimetaphosphimic acid,** because the analyses of the barium and silver salts agreed equally well with pyrophosphoric diamide, $(NH_2)_2(HO)_2P_2O_3$, or with $(NH_2)_3(HO)_3P_3O_3+1\frac{1}{2}H_2O$. Triphosphimic acid is obtained by the hydrolysis of an ethereal soln. of triphosphonitrilic chloride, $P_3N_3Cl_3$, by an aq. soln. of sodium acetate. The decomposition of a cold aq. soln. of silver trimetaphosphimate also furnishes a soln. of the acid. The acid is extremely soluble in water; the aq. soln. does not crystallize on evaporation, but it furnishes a gum-like mass. The constitutional formula assigned to trimetaphosphimic acid depends upon the formula assigned to triphosphonitrilic chloride from which it is formed by hydrolysis. Among other possibilities, H. N. Stokes suggests:



The latter type of formula is preferred, in agreement with the fact that no salt is known with six atoms of sodium per mol of the sodium salt. The ordinary sodium trimetaphosphimate has three sodium atoms per mol; although a most unstable salt with four sodium atoms per mol has been obtained by using a very large excess of sodium hydroxide, this readily passes into the trisodium salt. **Trisodium trimetaphosphimate,** $P_3N_3O_6H_3Na_3.4H_2O$, crystallizes in rhombic prisms from its aq. soln. at temp. below 80°; if the temp. exceeds 80°, needle-like crystals of the monohydrate, $P_3N_3O_6H_3Na_3.H_2O$, are deposited. The same salt is obtained by heating the tetrahydrate at 100°. It is not known if the difference between the two sodium salts is any more fundamental than a mere difference in the water of crystallization. Two anhydrous **silver trimetaphosphimates** are known: **trisilver trimetaphosphimate,** $P_3N_3O_6H_3Ag_3$, separates in monoclinic plates when an excess of silver nitrate is slowly added to a soln. of the sodium salt acidified with nitric acid, and **hexasilver trimetaphosphimate,** $P_3N_3O_6Ag_6$, is formed as a white, voluminous powder by adding sodium trimetaphosphimate to an excess of an ammoniacal soln. of silver nitrate. The existence of this salt is taken to show that the acid is probably a derivative of metaphosphimic acid. H. N. Stokes suggested that the hydrogen atoms are labile, and that the two graphic ring formula represent tautomeric compounds.

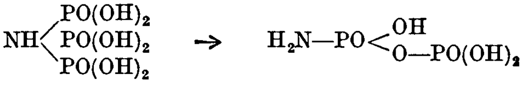
When an aq. soln. of trimetaphosphimic acid, or of one of its salts, acidified with one of the stronger mineral acids, is heated or kept for a long time, decomposition occurs—slowly if cold, rapidly if heated. Orthophosphoric acid and ammonia (ammonium phosphate) are the ultimate products of the decomposition. Several intermediate products have been detected; in addition to pyrophosphoric acid, what H. N. Stokes calls diimidotriphosphoric acid, and imidodiphosphoric acid have been found, and he represents the different stages of the decomposition:



Trimetaphosphimic acid, $(NH)_3(PO.OH)_3$ Diimidotriphosphoric acid, $(NH)_2.PO(OH).2PO(OH)_2$

Imidodiphosphoric acid, $NH.2PO(OH)_2$. Pyrophosphoric acid, $(HO)_4P_2O_3$. Orthophosphoric acid, H_3PO_4.

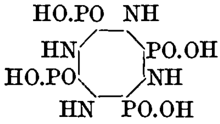
The hypothesis that imidodiphosphoric acid contains the group $\equiv P-NH-P\equiv$ explains very well its relationship with trimetaphosphimic acid, but it does not so readily explain its hydrolytic transformation into pyrophosphoric acid in view of the ease with which the latter passes into orthophosphoric acid, unless the fact be supplemented with the hypothesis that on account of the greater affinity of phosphorus for oxygen than for nitrogen, $PO(OH)_2$ can change places with a hydroxylic oxygen in the mol. $NH(PO(OH)_2)_2$ to form an unstable amidodiphosphoric acid:



$$NH{<}\begin{matrix}PO(OH)_2\\PO(OH)_2\\PO(OH)_2\end{matrix} \rightarrow H_2N-PO{<}\begin{matrix}OH\\O-PO(OH)_2\end{matrix}$$

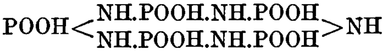
which then breaks down into pyrophosphoric acid. The last-named formula is virtually that given by J. H. Gladstone for amidophosphoric acid, and is equivalent to that required for imidodiphosphoric acid. An amido-imidodiphosphoric acid, $(OH)_2PO-NH-PO(OH)NH_2$, intermediate between diimidotriphosphoric acid and imidodiphosphoric acid, has not been detected among the products of the decomposition of trimetaphosphimic acid.

While the hydrolysis of triphosphonitrilic chloride furnishes trimetaphosphimic acid, the hydrolysis of tetraphosphonitrilic chloride, $P_4N_4Cl_8$, furnishes **tetrametaphosphimic acid,** $P_4N_4H_8O_8$, which, by analogy with trimetaphosphic acid, has the ring formula:



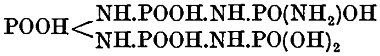
Tetraphosphimic acid crystallizes in colourless needles, with the composition $P_4N_4H_8O_8.2H_2O$. The acid is sparingly soluble in water—100 parts of water at 20° dissolve 0·64 part of the crystalline acid; the solubility is diminished if other acids be present; thus 10 per cent. of acetic acid lowers the solubility nearly 30 per cent. The aq. soln. is far more stable than the corresponding trimetaphosphimic acid; indeed, tetraphosphimic acid is more stable than any other acid of the series. Nitric acid readily transforms trimetaphosphimic acid into metaphosphoric acid in a few minutes, but the tetrametaphosphimic acid is scarcely attacked even by evaporation to dryness with conc. nitric acid or aqua regia. The acid usually behaves as if it were di-, tetra-, or octo-basic. The salts readily crystallize, and are usually sparingly soluble in water. Thus, **dipotassium tetrametaphosphimate,** $K_2H_6P_4N_4O_8$, is formed by dissolving the acid in a dil. soln. of potassium hydroxide, when prismatic crystals of the salt separate on adding acetic acid: **tetrapotassium tetrametaphosphimate,** $K_4H_4P_4N_4O_8$, forms sparingly soluble tablets. The dibarium salt crystallizes with the eq. of two mols of water; the tetrasodium salt with 2½ mols of water; the diammonium salt is anhydrous; and the tetrammonium salt has the eq. of four mols of water. **Tetrasilver tetrametaphosphimate,** $Ag_4H_4P_4N_4O_8$, separates as a white precipitate on adding silver nitrate to a soln. of the acid; with ammoniacal silver nitrate and a soln. of the ammonium salt, yellow **octosilver tetrametaphosphimate,** $Ag_8P_4N_4O_8$, is formed.

While the hydrolysis of triphosphonitrilic chloride with sodium acetate furnishes trimetaphosphimic acid; and the hydrolysis of tetraphosphonitrilic chloride with water furnishes tetrametaphosphimic acid, the hydrolysis of pentaphosphonitrilic chloride, $P_5N_5Cl_{10}$, with sodium hydroxide in ethereal soln. furnishes **sodium pentametaphosphimic acid,** $P_5N_5H_{10}O_{10}$, or rather the alkali pentametaphosphimate—sufficient alkali must be present to maintain the alkalinity of the soln. The sodium salts are amorphous, and are precipitated in a gelatinous form by the addition of alcohol to the alkaline soln., or to the soln. neutralized with acetic or nitric acid. Penta- and tetra-sodium salts and salts with even less sodium each with the equivalent of two mols of water of crystallization have been obtained. The silver salts of the meta-phosphimic acids are all anhydrous. The composition of the silver salts depends upon the relative amounts of the reacting substances. The salt $P_5N_5O_{10}H_5Ag_5$ is precipitated by adding silver nitrate to an acidified soln. of the sodium salt; salts with a higher proportion of silver are precipitated from ammoniacal soln. Salts with up to five atoms of silver per mol are white, and those containing more silver are yellow, and this the more the greater the proportion of silver they contain. The free acid, contaminated with some impurities, is obtained by decomposing the silver salt by hydrogen sulphide under well-cooled water. A soln. of the acid has a somewhat astringent taste, and is imperfectly precipitated by alcohol in a gelatinous form. The aq. soln. is more stable than trimetaphosphimic acid; and has a lower rate of decomposition when acted upon by nitric acid. Tetrametaphosphimic, triimidotetraphosphoric, diimidotriphosphoric, and orthophosphoric acids have been detected among the products of decomposition. Pentametaphosphimic acid is conveniently regarded as the lactam (that is, the anhydride of an amido-acid):



$$\mathrm{POOH}<\begin{matrix}\mathrm{NH.POOH.NH.POOH}\\ \mathrm{NH.POOH.NH.POOH}\end{matrix}>\mathrm{NH}$$

of *amidotetrimidopentaphosphoric acid:*



$$\mathrm{POOH}<\begin{matrix}\mathrm{NH.POOH.NH.PO(NH_2)OH}\\ \mathrm{NH.POOH.NH.PO(OH)_2}\end{matrix}$$

formed by the loss of a mol of water. The acid is said to exist in the lactam form in the pentasilver salt and in soln. of the acid and normal salts; in alkaline soln. the acid is thought to be in the open form because the silver salt prepared in an alkaline soln. has a composition corresponding with this formula.

H. N. Stokes found that **hexametaphosphimic acid,** $P_6N_6H_{12}O_{12}$, is obtained from hexaphosphonitrilic chloride, $P_6N_6Cl_{12}$, in a manner analogous with the preparation of pentametaphosphimic acid from pentaphosphonitrilic chloride. The hexa- and penta-metaphosphimic acids and their salts closely resemble one another, but the former are rather less stable than the latter. A hexa-sodium salt is obtained by treating a soln. of the acid neutralized with sodium hydroxide by alcohol. The hexasilver salt is obtained in a manner analogous with that employed for the corresponding salt of pentametaphosphimic acid; and a yellow salt is obtained by precipitation from an alkaline soln. The acid is regarded as the lactam (anhydride) of *amidopentimidohexaphosphoric acid,* that is

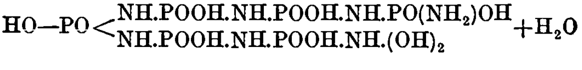
$$\mathrm{POOH}<\begin{matrix}\mathrm{POOH.NH.POOH.NH.POOH}\\ \mathrm{POOH.NH.POOH.NH.POOH}\end{matrix}>\mathrm{NH}$$

from

$$\mathrm{POOH}<\begin{matrix}\mathrm{POOH.NH.POOH.NH.PO(NH_2)OH}\\ \mathrm{POOH.NH.POOH.NH.PO(OH)_2}\end{matrix}$$

by the loss of a mol of water. When the sodium salt is heated with acetic acid it gives tetrametaphosphimic acid.

The hydrolysis of the higher homologues of the phosphonitrilic chlorides does not furnish corresponding metaphosphimic acids, for while hexaphosphonitrilic chloride furnishes hexametaphosphimic acid, heptaphosphonitrilic chloride, $P_7N_7Cl_{14}$, does not furnish heptametaphosphimic acid, but rather *amidohexaimidoheptaphosphoric acid—vide supra*—with the empirical formula $H_{16}P_7N_7O_{15}$, or $(PNO_2H_2)_7H_2O$, that is:



$$\mathrm{HO{-}PO}<\begin{matrix}\mathrm{NH.POOH.NH.POOH.NH.PO(NH_2)OH}\\ \mathrm{NH.POOH.NH.POOH.NH.(OH)_2}\end{matrix}+\mathrm{H_2O}$$

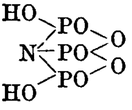
so that the homologous series of the phosphimic acids terminates with the acid

$(PNO_6H_2)_6$. The tri-, tetra-, penta-, and hexa-metaphosphamic acids may thus exist in two forms—the lactamic form, metaphosphimic acids, $(PNO_2H_2)_n$, where n is 3, 4, 5, or 6, which exists only in neutral or acidic soln.; and the open-chain form, $(PNO_2H_2)_n + H_2O$, which exists in alkaline soln. Acids derived from heptaphosphonitrilic chloride, and the higher members, do not appear to form lactams, and the open-chain form persists under all circumstances. The acid furnishes *sodium amidohexaimidoheptaphosphate*, $Na_7P_7N_7H_9O_{15}$, as a very soluble white powder, and *silver amidohexaimidoheptaphosphate*, $Ag_7P_7N_7H_9O_{15}$, as a sparingly soluble powder. The tri- and tetra-metaphosphimic acids give characteristic salts. The salts with five, six, and seven atoms of phosphorus have not been crystallized; alcohol precipitates the alkali salts from their aq. soln. as syrups which can be dehydrated to form amorphous powders. Trimetaphosphimic acid forms neutral sodium salts with three sodium atoms per mol; tetrametaphosphimic acid gives salts with two and four sodium atoms per mol; while the penta-acid gives a salt with five sodium atoms and which is strongly alkaline. The decreasing acidity of unneutralized hydroxyl-groups, well shown in orthophosphoric acid, is increasingly pronounced with the higher members of the metaphosphimic acids. The salts of the higher members of the series are readily hydrolyzed in aq. soln., and this, together with the feeble crystallizing powers, makes the preparation of even moderately pure salts very difficult.

H. N. Stokes mentioned *henametaphosphimic acid*, formed by hydrolysis from an oily liquid obtained in the preparation of the chloronitrides, with the composition $P_{11}N_{11}O_{22}$. The acid readily decomposes into diimidotriphosphoric, triimidotetraphosphoric, and tetrametaphosphimic acids.

Dry ammonia acts slowly on triphosphonitrilic chloride in ethereal soln., forming triphosphonitrilic chloramide, $P_3N_3(NH_2)_2Cl_4$, which remains in soln. The reaction slowly progresses yet further, but not to completion. The products of the further action are insoluble in ether. When the ethereal soln. of the chloramide is hydrolyzed with sodium hydroxide, **sodium diamidotrimetaphosphimate** is formed. Conc. aq. ammonia reacts vigorously with the tri-, tetra-, and the pentaphosphonitrilic chlorides in ethereal soln., and an indefinite proportion of the chlorine is replaced by amido-groups. Amido-compounds of constant composition have accordingly not been prepared.

According to A. Mente, if in the preparation of imidodiphosphoric acid, the products be heated to 290° or 300°, ammonia is evolved, and a white fiocculent powder is formed from which ammonium chloride can be removed by washing with water. The pale yellow residue dissolves in aq. ammonia; and when the soln. is acidified with nitric or hydrochloric acid, a white precipitate is formed, and the soln. contains what is thought to be **nitrilotrimetaphosphoric acid,**



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The intermediate stages of the reaction are indicated by the scheme: $NH(POCl_2)_2 \rightarrow N(POCl_2)_3$, and this product, on hydrolysis, furnishes the acid in question. The free acid cannot be isolated, though lead, barium, and silver salts can be readily obtained. The alkali salts are crystalline and soluble in water. Oxidizing agents convert the soln. into orthophosphates.

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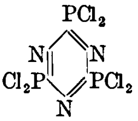
[1] A. Mente, *Liebig's Ann.*, 248. 232, 1888; J. H. Gladstone, *Journ. Chem. Soc.*, 2. 121, 1850; 3. 135, 353, 1851; 22. 15, 1869; H. N. Stokes, *Amer. Chem. Journ.*, 15. 198, 1893; 16. 123, 140, 1894; 17. 275, 1895; 18. 629, 1896; 20. 740, 1898; *Zeit. anorg. Chem.*, 19. 42, 1899.

§ 72. Phosphorus Chloronitrides or Phosphonitrilic Chlorides

In the attempt to prepare the amides of phosphoric acid by the action of gaseous ammonia or ammonium chloride on phosphorus pentachloride, J. von Liebig,[1] in 1832, discovered a remarkable compound which he called *Chlorphosphorstickstoff* —remarkable because it was not expected that the compound would be so stable as to enable it to be distilled in steam, or boiled with acids or alkalies without appreciable decomposition. Analyses led J. von Liebig to the formula $P_3N_2Cl_5$, but A. Laurent, and C. Gerhardt showed that the empirical formula must be $PNCl_2$; and, in 1864, J. H. Gladstone and J. D. Holmes tripled Laurent and Gerhardt's formula so as to make it harmonize with the vap. density. H. Wichelhaus then suggested a constitutional cyclic formula :

to explain its stability; but H. N. Stokes argued that since (1) the compound decomposes into orthophosphoric acid and ammonia, (2) it is formed from ammonia and phosphorus pentachloride ; and (3) there are no signs of double or triple-linked phosphoric acids or of hydrazine in the decomposition products, the probability is that the phosphorus atoms are united by nitrogen atoms. He also believed that the absence of hydroxylamine in the decomposition products shows that the chlorine is probably united directly to the phosphorus and not to the nitrogen atoms. In agreement with these arguments, H. N. Stokes prefers the cyclic formula :



He has also shown that this compound—now called triphosphonitrilic chloride, $N_3P_3O_6H_6$—is the first member of a series of polymers with the general formula $(PNCl_2)_n$, where n ranges from 3 to 7 and upwards. The more important physical constants of these compounds, mainly investigated by H. N. Stokes, are indicated in Table XXXV. No member of the series lower than the triphosphonitrilic chloride has been obtained. Each member of the series can be converted by heat into a rubber-like polyphosphonitrilic chloride or mixture of these chlorides of high mol. wt. and which are highly elastic, and insoluble in neutral solvents, but swell up considerably in benzene. On distillation at a higher temp., the higher members break down into the lower members, which can then be separated by fractional distillation. The polymerization of any member of the series begins at about 250°, and is almost instantaneous at about 350° ; depolymerization begins just over 350°, and is rapid near incipient redness.

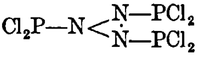
Table XXXV.—Physical Properties of the Phosphonitrilic Chlorides.

Phosphonitrilic chloride formula.	Melting point.	Boiling point at 13 mm.	Boiling point 760 mm.
Triphosphonitrilic chloride, $(PNCl_2)_3$.	114°	127°	256·5°
Tetraphosphonitrilic chloride, $(PNCl_2)_4$.	123·5°	188°	328·5°
Pentaphosphonitrilic chloride, $(PNCl_2)_5$.	40·5°–41°	223°–224·3°	polymerizes
Hexaphosphonitrilic chloride, $(PNCl_2)_6$.	90°	261°–263°	polymerizes
Heptaphosphonitrilic chloride, $(PNCl_2)_7$.	below −18°	289°–294°	polymerizes
Polyphosphonitrilic chloride, $(PNCl_2)_n$.	below 500°	depolymerizes	on distillation

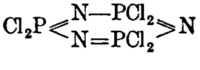
The preparation of the phosphonitrilic chlorides.—Equimolecular parts of ammonium chloride and phosphorus pentachloride are gradually heated in a sealed tube to 150°—frequently opening the tube to allow the escape of the hydrogen chloride, and prevent the development of too great a pressure. A reaction $n\mathrm{NH_4Cl}+n\mathrm{PCl_5}=(\mathrm{PNCl_2})_n+4n\mathrm{HCl}$ occurs. The contents of the tube are extracted with gasoline, and the insoluble residue is distilled by heating to incipient redness. The distillate is a crystalline mass permeated with a yellow oil. The mass is washed with hot water, and afterwards distilled at 200° (13–15 mm.) in a sublimate flask, since the distillate solidifies on cooling. This fraction contains the tri- and the tetra-phosphonitrilic chlorides ; the residue in the retort contains the higher members of the series. The distillate is re-fractionated, and crystallized from benzene three or four times ; the tetraphosphonitrilic chloride accumulates in the mother-liquid. The residue in the flask, boiling over 200° (13–15 mm.), is fractionally distilled at 13–15 mm. press. On redistilling the fractions, penta-, hexa-, and hepta-phosphonitrilic chlorides are obtained. The hexa-compound is contaminated with a compound $\mathrm{P_6N_7Cl_9}$, from which it is separated by fractional crystallization from benzene—the hexaphosphonitrilic chloride is the less soluble.

Instead of using the troublesome process of H. N. Stokes, R. Schenck and G. Römer added 120–130 grms. of ammonium chloride to a soln. of 400 grms. of phosphorus pentachloride in a litre of *s*-tetrachloroethane, and boiled the mixture in a reflux condenser at 135° until hydrogen chloride is no longer evolved from the calcium chloride tube at the top of the condenser. In about 20 hrs., the ammonium chloride is filtered off, and the solvent distilled off at about 11 mm. press. The residue is a buttery mass free from ammonium chloride. The yield, 220 grms., is nearly theoretical. The oil is removed by suctional filtration, and the last portions by benzene at 0°. About 100 grms. of mixed tri- and tetra-phosphonitrilic chlorides remain as a crystalline powder. This is recrystallized from benzene, fused at about 50°, and distilled under reduced press. At 10 mm. press., 75 grms. of the tri-polymer distil at 124°, and 25 grms. of the tetra-polymer at 185°. These are recrystallized from benzene or chloroform.

According to H. N. Stokes, the first member of the series, **triphosphonitrilic chloride,** $\mathrm{P_3N_3Cl_6}$, forms large thick rhombic crystals of sp. gr. 1·98. R. Schenck and G. Römer said that this compound boils at 124° and 10 mm., and melts at 114° ; and that it polymerizes to a colourless transparent mass resembling caoutchouc at temp. above 255°. H. N. Stokes found that it is soluble in ether, chloroform, benzene, carbon disulphide, etc. 100 grms. of ether at 20° dissolve 46·5 grms. of the solid, and 100 grms. of benzene at the same temp. 57·4 grms. The solid readily dissolves in glacial acetic acid, and in sulphuric acid ; when the latter soln. is boiled, a vapour with a pleasant aromatic odour is evolved, which soon attacks the respiratory passages, and makes breathing difficult. Although not readily attacked by water alone, it is hydrolyzed when a soln. in alcohol-free ether is shaken with water. The final product of the action is trimetaphosphimic acid, $\mathrm{P_3N_3(OH)_6}$, in which all the chlorine is replaced by hydroxyl ; an intermediate product of the hydrolysis, **triphosphonitrilic hydroxylchloride,** $\mathrm{P_3N_3Cl_4(OH)_2}$, has been isolated in well-defined, minute, prismatic crystals; other hydroxychlorides are probably formed at the same time. Orthophosphoric acid, ammonia, and hydrochloric acid are ultimate products of the hydrolysis. Aniline or piperidine transform the benzene soln. into the anilide $\mathrm{N{\equiv}P(NHC_6H_5)_2}$, melting at 261°, and the piperidide melting at 231°. R. Schenck found that cryoscopic and ebulliscopic methods show that the product of the action of aniline has the formula $\{\mathrm{NP(NHC_6H_5)_2}\}_3$. F. Wissemann studied its action on methyl and ethyl alcohols, benzyl and acetoacetic ethers, phenol, α-naphthol, and of hydrocyanic acid in pyrodine and quinoline soln. ; and H. Schäperkötter, the action on tertiary amines, amino-acid esters, and ammonia. Water in the presence of piperidine converts these compounds into pyridine hydrochloride and pyridinium metaphosphimate, $\mathrm{N{\equiv}P(OH)_2.C_5H_5N}$. All the pyridine is expelled at 200° and 11 mm. press., leaving a residue of metaphosphimic acid. It is thought that neither of the closed-ring formulæ



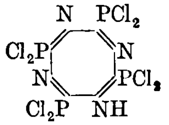
$$\mathrm{Cl_2P{-}N}<\genfrac{}{}{0pt}{}{\mathrm{N{-}PCl_2}}{\dot{\mathrm{N}}\mathrm{{-}PCl_2}}$$



$$\mathrm{Cl_2P}<\genfrac{}{}{0pt}{}{\mathrm{N{-}PCl_2}}{\mathrm{N{=}PCl_2}}>\mathrm{N}$$

adequately explained the reactions. According to A. Besson and G. Rosset, when triphosphonitrilic chloride is treated with liquid ammonia, one-third of the chlorine is replaced by an amido-group, forming white **triphosphonitrilic amide,** $P_3N_3(NH_2)_6$. This compound, when heated to about 220° for some days, loses ammonia, and furnishes phospham, PN_2H. If dry ammonia gas is passed into a soln. of triphosphonitrilic chloride in carbon tetrachloride, slender, prismatic, needle-like crystals of **triphosphonitrilic chloramide** are obtained, possibly $P_3N_3Cl_4(NH_2)_2$ are formed. The compound is insoluble in ether and carbon disulphide,and is probably an intermediate product in the action of ammonia on triphosphonitrilic chloride. Sulphur trioxide and nitrogen peroxide also form additional products with triphosphonitrilic chloride. When heated with nitrogen peroxide in a sealed tube to 20°–25°, triphosphonitrilic chloride forms a compound with the ultimate composition $P_4O_{12}N$, corresponding with $2P_2O_5.NO_2$—*vide supra.* The same compound is formed by heating phosphorus pentoxide with nitrogen peroxide in a sealed tube to 200°. It is sparingly soluble in water, and the aq. soln. quickly decomposes. According to A. Besson, also, when the compound of phosphorus pentachloride with ammonia is slowly heated, it loses ammonia, and, between 175° and 230° under a reduced press. (50 mm.), white crystals of what has been called **phosphorus dichloronitride,** $(PCl_2N)_n$, sublime. This compound is probably identical with H. N. Stokes' triphosphonitrilic chloride. The crystals, purified by resublimation in vacuo, melt at 106°, and are distinctly volatile under reduced press. at 100°, so that the compound does not preexist in the octammine from which it was prepared, for the latter does not form a sublimate below 175°.

The next member of the series, **tetraphosphonitrilic chloride,** $P_4N_4Cl_8$, forms colourless prisms with a sp. gr. 2·18. R. Schenck and G. Römer gave 185° for the b.p. at 10 mm. press., and 123·5° for the m.p., and added that above 255° it behaves like the tri-polymer. H. N. Stokes found that analyses, vapour density determinations in dry hydrogen, and the depression of the f.p. of benzene soln., agree with the formula $P_4N_4Cl_8$ and by analogy with triphosphonitrilic chloride, the constitution may be:



It dissolves in similar solvents to form the triphosphonitrilic chloride—thus, 100 grms. of ether at 20° dissolve 12·3 grms. of the compound; and 100 grms. of benzene, 20·9 grms. It is scarcely attacked by boiling water, acids, or alkali-lye, but water acts upon the ethereal soln. rather more slowly than is the case with the preceding compound, and forms tetrametaphosphamic acid, $P_4N_4(OH)_8.2H_2O$; an intermediate **tetraphosphonitrilic hydroxychloride** has been obtained. R. Schenck and G. Römer obtained similar reactions with aniline and piperidine to those obtained with the tripolymer. While the oily phosphonitrilic chlorides are thought to be open-chain products, the tri- and tetra-polymers are thought to be closed-chain compounds. According to R. Schenck, cryoscopic and ebulliscopic methods show that the product of the action of aniline has the composition $\{NP(NHC_6H_5)_2\}_4$. F. Wissemann studied the action of tetraphosphonitrilic chloride on methyl and ethyl alcohols, benzyl acetoacetic ethers, phenol, α-naphthol, and of hydrocyanic acid in pyridine and quinoline soln.; and H. Schäperkötter, the action on tertiary amines, amino-acid esters, and ammonia.

The next member of the series, **pentaphosphonitrilic chloride,** $P_5N_5Cl_{10}$, was found by H. N. Stokes to form a crystalline mass readily soluble in various organic solvents. It is readily attacked by water in ethereal soln. giving pentametaphosphimic acid. It is precipitated by water from its soln. in glacial acetic acid. Analyses and its effect on the b.p. of benzene soln. agree with the formula $P_5N_5Cl_{10}$. A. M. Vasilieff modifying the definition of a eutectic regarded the pentametaphosphonitrilic chloride as a eutectic: $(PNCl_2)_4+(PNCl_2)_6=2(PNCl_2)_5$. Finally,

H. N. Stokes found that **hexaphosphonitrilic chloride,** $P_6N_6Cl_{12}$, forms long, prismatic rhombic crystals. It gives hexametaphosphimic acid when its ethereal soln. is shaken with water, and is but slowly attacked by boiling water alone. Hydrogen chloride is slowly evolved when it is exposed to moist air. Analyses and the b.p. of benzene soln. correspond with the formula $P_6N_6Cl_{12}$. **Heptaphosphonitrilic chloride,** $P_7N_7Cl_{14}$, is a colourless, viscid liquid readily miscible with organic solvents, and it behaves similarly with the other phosphonitrilic chlorides towards water; its mol. wt. has been established by analyses, and its effect on the b.p. of benzene.

The oily residue remaining after the above compounds have been removed by distillation is doubtless a mixture of higher polymerides. **Hexaphosphoheptanitrilic chloride,** $P_6N_7Cl_9$, resembles the phosphonitrilic chlorides in its general properties; it fuses at 237·5°, and boils at 251°–261° (13 mm.) without change. It forms transparent rhombic prisms. Analyses and mol. wt. determinations in boiling benzene agree with the formula $P_6N_7Cl_9$. It may be hexaphosphonitrilic chloride in which three atoms of chlorine have been replaced by one of nitrogen.

A series of **phosphonitrilic bromides,** $(PNBr_2)_n$, analogous with the phosphonitrilic chlorides, have been made by the action of ammonia on phosphorus pentabromide. The phosphonitrilic bromide, $(PNBr_2)_3$, forms colourless rhombohedral crystals which melt at 188°–190°, and are insoluble in water. A. Besson obtained white crystals of the *phosphorus dibromonitride,* $(PBr_2N)_n$, or **triphosphonitrilic bromide,** in a somewhat similar manner to that employed for the corresponding chloride. The crystals melt at 188°–190°, and sublime in vacuo at 150°. This compound is insoluble in water, fairly soluble in ether, and less soluble in carbon disulphide and chloroform.

The antimony analogues of the phosphorus chloronitriles, produced by the action of ammonium chloride on phosphorus pentachloride, have not been prepared; instead of furnishing the analogous **antimony chloronitride,** $SbCl_5+NH_4Cl=SbNCl_2+4HCl$, the main reaction proceeds: $3SbCl_5+2NH_4Cl=3SbCl_3+8HCl+N_2$, showing that the antimonic chloride is reduced to the lower chloride—presumably the primary reaction is a decomposition of ammonium chloride by chlorine from dissociated antimony pentachloride. Ferric, cupric, and chromic chlorides under similar conditions are also reduced to the lower chlorides. This agrees with the general rule that only those metal chlorides which readily dissociate to a lower chloride when heated with ammonium chloride in a sealed tube, break up the ammonium salt liberating nitrogen. Mercuric chloride is exceptional in that it forms a double salt under similar conditions. With titanium and tin tetrachlorides there is no corresponding dissociation under the conditions of the experiment, and no reaction occurs other than the formation of a double salt. E. and P. Fireman tried also to prepare analogues of the polymeric phosphonitrilic chlorides with antimony or tin in place of phosphorus, and phosphorus in place of nitrogen by the action of phosphonium iodide, PH_4I, on antimony pentachloride, or tin tetrachloride. The action of phosphonium iodide is, however, radically different from that of ammonium chloride, since it acts as a reducing agent. When phosphonium iodide and antimony pentachloride are brought into contact, a reaction occurs with explosive violence, but when the two compounds are brought together in a sealed tube, and heated for say 5 hrs. between 95° and 105°, the pentachloride is reduced to the trichloride, and a third of the antimony is converted into the tri-iodide: $3SbCl_5+3PH_4I=SbI_3+2SbCl_3+9HCl+PH_3+2P$; and with phosphorus trichloride under similar conditions, the reaction is symbolized: $3PCl_5+3PH_4I=PI_3+PCl_3+12HCl+4P$. Stannic chloride, and phosphonium iodide under similar conditions furnish stannous chloride and iodide: $6SnCl_4+6PH_4I=3SnCl_2+3SnI_2+18HCl+2PH_3+4P$.

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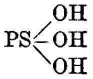
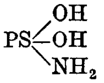
§ 73. Ammonia Derivatives of Thiophosphoric Acid

Ammonia derivatives of thiophosphoric acid, $PS(OH)_3$, have been reported in which the hydroxyl groups are replaced one by one by the amido-radicle; thus:



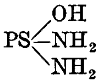
$$\mathrm{PS}\!\begin{array}{l}\diagup\mathrm{OH}\\ -\mathrm{OH}\\ \diagdown\mathrm{OH}\end{array}$$

Thiophosphoric acid.



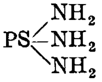
$$\mathrm{PS}\!\begin{array}{l}\diagup\mathrm{OH}\\ -\mathrm{OH}\\ \diagdown\mathrm{NH_2}\end{array}$$

Amidothiophosphoric acid.



$$\mathrm{PS}\!\begin{array}{l}\diagup\mathrm{OH}\\ -\mathrm{NH_2}\\ \diagdown\mathrm{NH_2}\end{array}$$

Diamidothiophosphoric acid.



$$\mathrm{PS}\!\begin{array}{l}\diagup\mathrm{NH_2}\\ -\mathrm{NH_2}\\ \diagdown\mathrm{NH_2}\end{array}$$

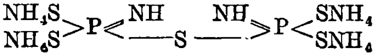
Thiophosphoryl amide.

J. H. Gladstone and J. D. Holmes[1] agitated dil. aq. ammonia with thiophosphoryl chloride, and obtained an acid liquor which contained ammonium chloride and **amidothiophosphoric acid,** $SP(NH_2)(OH_2)$, and from which the cadmium or lead salts could be precipitated, but not the salts of the alkaline earths, or of iron, nickel, or cobalt. Mercuric chloride gave a yellow thiochloride which became black when treated with acid.

J. H. Gladstone and J. D. Holmes prepared **diamidothiophosphoric acid,** $SP(NH_2)_2(OH)$, by the action of ammonia gas on thiophosphoryl chloride, and digesting the product in water. T. E. Thorpe and J. W. Rodger obtained it by the action of ammonia on thiophosphoryl fluoride, and digesting the product in water: $SP(NH_2)_2F+H_2O=HF+SP(NH_2)_2OH$. The acid liquor gives the reactions neither of hydrogen sulphide nor of phosphoric acid. After neutralization, the soln. gives white, flocculent precipitates with zinc and cadmium salts; a greenish-white precipitate with a nickel salt; and a bluish-white one from a cobalt salt. The precipitates are soluble in aq. ammonia and in acids. Aq. soln. of lead chloride give a white precipitate soluble in dil. nitric acid, and when the precipitate is heated with water, it blackens. The neutralized aq. soln. gives a yellowish-white precipitate with a soln. of a copper salt; the precipitate becomes brown when dried, and it is soluble in an aq. soln. of potassium cyanide, but not in dil. acids or aq. ammonia. A soln. of stannous chloride gives a white precipitate; and one of mercuric chloride, a white precipitate which soon passes into yellow mercuric thiochloride. No precipitates are produced with soln. of calcium, barium, magnesium, aluminium, or ferric salts. The metal salts decompose when heated, forming ammonia, and ammonium sulphide. The soln. obtained by mixing silver or copper salts with an aq. soln. of the acid, decompose when evaporated over conc. sulphuric acid with the separation of sulphur.

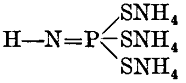
H. Schiff,[2] and M. Chevrier reported **thiophosphoryl amide,** $SP(NH_2)_3$, to be formed along with ammonium chloride when ammonia is passed over thiophosphoryl chloride; the white solid first formed is pulverized and again exposed to the action of the gas. The product is rapidly extracted with water, and thiophosphoryl amide remains as a white (H. Schiff), or yellowish-white (M. Chevrier), amorphous mass of sp. gr. 1·7 at 13°. When heated over 200°, ammonium hydrosulphide is evolved, and at 240°, about 20 per cent. of sulphur is formed. H. Schiff said that if heated out of contact with air, the residue is free from sulphur and is probably phospham. According to H. Schiff, the compound is rapidly decomposed by water, particularly if warm, forming hydrogen sulphide, and also, according to M. Chevrier, ammonium thiophosphate. Fuming nitric acid oxidizes the triamide vigorously to phosphoric and sulphuric acids; and with potassium hydroxide, ammonia is evolved. The triamide is sparingly soluble in alcohol, ether, and carbon disulphide. The Zircon Glühlampenwerk tried the triamide in making filaments for incandescent electric lamps.

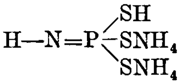
According to A. Stock and B. Hoffmann, phosphorus pentasulphide and ammonia at ordinary temp. form a yellow addition product, $P_2S_5.6NH_3$, and at $-20°$, a colourless addition product $P_2S_5.7NH_3$. The hexammine is considered to be ammonium diimidopentathiodiphosphate:

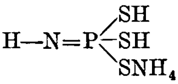


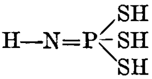
$$\begin{array}{l}\mathrm{NH_4S}\\ \mathrm{NH_4S}\end{array}\!>\mathrm{P}<\!\begin{array}{c}\mathrm{NH}\qquad\mathrm{NH}\\ \text{——}\mathrm{S}\text{——}\end{array}\!>\mathrm{P}<\!\begin{array}{l}\mathrm{SNH_4}\\ \mathrm{SNH_4}\end{array}$$

while the heptammine is regarded as a mixture of ammonium nitrilodithiophosphate and ammonium imidotrithiophosphate derived from the diimidopentathiodiphosphate: $NH_3+(NH_4S)_2P(NH).S.P(NH)(SNH_4)_2 \rightarrow NP(SNH_4)_2+HN.P(SNH_4)_3$. The ammonium imidotrithiophosphate can lose ammonia in successive stages to form a series of imidotrithiophosphoric acids, HN : P(SH)$_3$, thus:


Triammonium imidotrithio-phosphate.


Diammonium imidotri-thiophosphate.

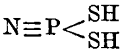

Ammonium imidotrithio-phosphate.


Imidotrithiophosphoric acid.

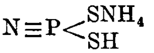
These three ammonium salts, and the free acid, when heated may pass into thiophosphoryl nitrile, and at a red-heat into phosphorus nitride. When diammonium nitrilodithiophosphate is heated, it loses ammonia, forming the monammonium salt —the free acid, nitrilodithiophosphoric acid, N ⋮ P(SH)$_2$, has not been made:

$N\equiv P=S$

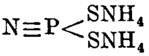
Thiophosphoryl nitrile.


$N\equiv P<\begin{smallmatrix}SH\\SH\end{smallmatrix}$

Nitrilodithiophosphoric acid.


$N\equiv P<\begin{smallmatrix}SNH_4\\SH\end{smallmatrix}$

Ammonium nitrilo-dithiophosphate.


$N\equiv P<\begin{smallmatrix}SNH_4\\SNH_4\end{smallmatrix}$

Diammonium nitrilo-dithiophosphate.

E. Glatzel obtained **thiophosphoryl nitrile,** N ⋮ P : S, by heating a mixture of 3 mols of phosphorus pentasulphide, and one mol of ammonium chloride: $2NH_4Cl+P_2S_5=2NPS+2HCl+3H_2S$. A. Stock and co-workers obtained it by heating one of the ammonium imidotrithiophosphates in vacuo. The decomposition begins at 180°, but the temp. should be carried to 325° very slowly in order to complete the reaction. It is also formed by heating imidotrithiophosphoric acid to 250°–280°, in vacuo; or ammonium diamidopentathiodiphosphate to 270° in vacuo. The white product is stable; it is very slowly attacked by water; and quickly by hot dil. hydrochloric acid. When heated to 140° with water in a sealed tube it is completely decomposed: $NPS+4H_2O=H_3PO_4+H_2S+NH_3$. Red or fuming, warm nitric acid attacks the nitrile. Liquid ammonia has no action on the nitrile-group, but at high temp., phosphorus pentasulphide and nitride are formed.

A. Stock and co-workers were unable to isolate **nitrilodithiophosphoric acid,** N ⋮ P(SH)$_2$, because when its salts are treated with acids, the product decomposes instantly into phosphoric acid, hydrogen sulphide, and ammonia. No reaction occurs when the salts are boiled with alkali-lye. A. Stock and co-workers found that **ammonium hydronitrilodithiophosphate,** $NP(SH)SNH_4$, is obtained by heating the diammonium salt in vacuo at 100°; and by heating the product of the action of liquid ammonia on phosphorus pentasulphide to 125°. The product is a white crystalline mass, which has an odour of hydrogen sulphide when exposed to moist air; at 180°–200° in a current of an indifferent gas, or in vacuo, the ammonium salt yields ammonia and hydrogen sulphide; at 300°, thiophosphoryl nitrile; and at 800°, phosphorus nitride. A. Stock and co-workers found that **ammonium nitrilodithiophosphate,** $NP(SNH_4)_2$, is produced along with ammonium imidotrithiophosphate by the action of liquid ammonia on phosphorus pentasulphide or phosphorus hexamminopentasulphide; or by passing ammonia over phosphorus pentasulphide. The ammonium imidotrithiophosphate is very sparingly soluble in liquid ammonia and crystallizes out, while the ammonium nitrilodithiophosphate dissolves in that menstruum, and is obtained by evaporating off the solvent. The colourless product is soluble in liquid ammonia, and when this soln. is evaporated, the ammonium salt remains as a white resinous mass. When the salt is heated it furnishes a voluminous grey powder and finally phosphorus nitride. At 100°, in vacuo, it loses a mol of ammonia, forming the primary salt; at 180°–200° in vacuo or in a current of an indifferent gas, it behaves like the monammonium salt. It is easily soluble in water. When a mixed soln. of the diammonium salt and potassium hydroxide is treated with alcohol, an oily mass of

potassium nitrilodithiophosphate, $NP(SK)_2.nH_2O$, is produced, which does not crystallize when cooled in a freezing mixture. A similar product was obtained with the calculated quantity of sodium hydroxide, but, when cooled, the oil formed a mass of radiating needles of **sodium nitrilodithiophosphate**, $NP(SNa)_2.nH_2O$; a similar product was obtained by the action of sodium sulphate on the lead salt. When the soln. is treated with a lead salt, yellow **lead nitrilodithiophosphate**, NPS_2Pb, is formed ; with barium hydroxide, a voluminous, white mass of **barium nitrilodithiophosphate**, $NPS_2Ba.H_2O$, is produced.

A. Stock and co-workers found that when ammonium imidotrithiophosphate is heated in an atm. of hydrogen sulphide, **imidotrithiophosphoric acid**, $HN : P(SH)_3$, is formed: $NHP(SNH_4)_3+3H_2S=3NH_4SH+NHP(SH)_3$. The reaction begins at about 90°, and is continued for 12 hrs. at 140°–145°, and completed in several days at 175°–180°. The acid is pale yellow, and it becomes darker when heated and paler when cooled. It sp. gr. is 1·78 at 16·5°. No solvent is known which does not at the same time decompose the acid. It is insoluble in carbon disulphide even at 200° ; and it is hydrolyzed by water: $HNP(SH)_3+3H_2O=2H_2S+OP(OH)_2(SNH_4)$. The acid loses hydrogen sulphide at a high temp. ; and at 210°, it forms ammonium diimidopentathiodiphosphate. Liquid ammonia converts the acid into the triammonium salt ; gaseous hydrogen chloride has no action on the acid at ordinary temp., but with liquid hydrogen chloride, it forms **hydrochloroimidotrithiophosphoric acid**, $NP(SH)_3.HCl$, which gives off hydrogen chloride at 125° ; and with water forms sulphur and hydrogen sulphide. A. Stock and co-workers made **triammonium imidotrithiophosphate**, $HNP(SNH_4)_3$, along with diammonium nitrilotrithiophosphate by the action of liquid ammonia on phosphorus pentasulphide or hexamminopentasulphide : the imidotrithiophosphate is insoluble in liquid ammonia, the other product is soluble. The salt is obtained by the action of liquid ammonia on the free acid ; and by heating phosphorus with a soln. of sulphur in liquid ammonia at 100° when the brown soln. deposits this salt on standing. A similar result is obtained by dissolving phosphorus hexasulphide in liquid ammonia. The triammonium salt is a white, crystalline mass. The crystals are hygroscopic, and in dry air effloresce owing to the loss of ammonia ; but they can be preserved in sealed tubes. The salt is very sparingly soluble in liquid ammonia, and the solubility is but little affected even by raising the temp. to 100°. The salt is soluble in no other known organic or inorganic solvent without chemical change. The aq. soln. has an alkaline reaction, and the salt is hydrolyzed, for the imido-group is displaced by oxygen so that the liquid gives the reaction of the thiophosphates ; after some hours, the liquid smells of hydrogen sulphide, and it then reacts with a nitroprusside. If the aq. soln. be treated with alcohol, ammonium trithiophosphate is precipitated. The salt loses a mol of ammonia when heated in vacuo at 50°, and it is transformed into the diammonium salt ; and when heated to a high temp., phosphorus nitride is formed. When heated in an atm. of hydrogen sulphide, the ammonium salt is converted into the free acid. When the salt is treated with sodammonium in a sealed tube, **trisodium imidotrithiophosphate**, $NHP(SNa)_3$, is formed : $NHP(SNH_4)_3+3Na=HNP(SNa)_3+3NH_3+3H$. A. Stock and co-workers prepared diammonium imidotrithiophosphate, $NHP(SH)(SNH_4)_2$, by heating the triammonium salt in vacuo at 50° ; and by leaving the triammonium salt in vacuo over conc. sulphuric acid for 7 days. If the triammonium salt be treated with sodium ethoxide, **disodium imidotrithiophosphate**, $NHP(SH)(SNa)_2$, is formed. When the diammonium salt is heated in vacuo at 100°, it forms **ammonium imidotrithiophosphate**, $NHP(SH)_2(SNH_4)$.

A. Stock and co-workers obtained impure **diimidopentathiodiphosphoric acid**, $S\{P(SH)_2 : NH\}_2$, by heating imidotrithiophosphoric acid for a long time at 210°. It is suggested that *phosphoryl diimidosulphide*, $S\{PS(NH)_2\}_2$, is formed as an intermediate product of the decomposition at about 100°. They obtained **ammonium diimidopentathiodiphosphate**, $S\{P(SNH_4)_2 : (NH)\}_2$, by the action of ammonia at ordinary temp. on phosphorus pentasulphide ; and also by adding

3 grms. of the powdered sulphide to 12 c.c. of liquid ammonia near its b.p., and evaporating the ammonia from the yellow soln. The product is a yellow, hygroscopic solid which when heated to a high temp. furnishes phosphorus nitride; in vacuo, at 270°, it yields thiophosphoryl nitrile. The yellow soln. produced by cold water deposits sulphur, and has an odour of ammonium sulphide; the freshly prepared soln. does not give the reactions of phosphoric acid. The soln. in liquid ammonia forms ammonium imidotrithiophosphate and nitrilodithiophosphate as indicated above.

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[2] A. Stock and B. Hoffmann, *Ber.*, 36. 314, 898, 1903; A. Stock, B. Hoffmann, F. Müller, H. van Schönthan, and H. Küchler, *ib.*, 39. 1967, 1906; H. Schiff, *Liebig's Ann.*, 101. 303, 1857; *Journ. prakt. Chem.*, (1), 71. 161, 1857; M. Chevrier, *Compt. Rend.*, 66. 748, 1868; E. Glatzel, *Zeit. anorg. Chem.*, 4. 186, 1893; Zircon Glühlampenwerk, *German Pat.*, *D.R.P.* 210326, 1906.

CHAPTER L

PHOSPHORUS

§ 1. The History of Phosphorus

Phosphorus is one of the most remarkable of the many remarkable substances known to the chemist. The curious method of its discovery, the universality of its distribution, its intimate connection with the phenomena of animal and vegetable life, its extraordinary physical properties and chemical activity, its abnormal molecular constitution, the protean ease of its allotropic transformation, all combine to make up a history which abundantly justifies its old appellation of the *phosphorus mirabilis.*—T. E. THORPE.

ACCORDING to F. Licetus,[1] somewhere near the beginning of the seventeenth century a boot-maker, V. Casciarolus or Casciorolus, found a stone on Mons Padernus, Bologna, which was so heavy that he thought it contained a heavy metal. He found that after the stone—barytes—had been calcined in a charcoal fire and cooled, it glowed in darkness with a reddish light. It was called *litheosphorus*, or *litheophorus*; and also *Bologna stone* or *lapis bononiensis*. Some years later, C. A. Baldewein discovered another variety which he called *phosphorus hermeticus*, or *magnes luminaris*; and which came to be known as *Baldwin's phosphorus* (*q.v.*). In the seventeenth century, the term phosphorus—from *φῶς*, light; *φέρω*, I bear—was applied to designate any substance which was capable of becoming luminous in the dark.

J. von Kunckel related in his *Laboratorium chymicum* (Hambourg, 1716) that he heard that Hennig Brand, whom he ironically called a *doctor teutonicus*, had prepared a kind of phosphorus which gave a continuous glow in darkness; without being illumined by any lucid substance. G. W. von Leibniz, in his *Historia inventionis phosphori* (Berlin, 1710), said that H. Brand was an impoverished merchant who sought to restore his wealth by converting base metals into gold; and during his alchemical experiments with urine discovered phosphorus, *zufällig*. A letter from H. Brand to G. W. von Leibniz, published by H. Peters,[2] makes it appear that H. Brand first prepared phosphorus in 1669. J. D. Kraft bought the secret from H. Brand for 200 thalers, on condition that it was not communicated to J. von Kunckel. J. von Kunckel, however, did learn that H. Brand's phosphorus was obtained from urine; and soon afterwards discovered the mode of preparation. The properties of the newly discovered phosphorus were first described in a dissertation: *Noctiluca constans et per vices fulgurans, diutissime quæsita, nunc reperta* (Wittenberg, 1676), by J. von Kunckel's friend, G. Kirchmaier, in 1676; in J. S. Elsholz's *De phosphorisquatuor observatio* (Berlin, 1676); and in G. Schulze's *De phosphoro liquido, observatio* (Berlin, 1677). Shortly afterwards, J. von Kunckel described this substance in his *Oeffentliche Zuschrift vom Phosphoro mirabili und dessen leuchtenden Wunderpilulen* (Leipzig, 1678). About 1677, J. D. Kraft exhibited this wonderful *das kalte Feuer*, or *das immerwährende Feuer*, to various crowned heads in Europe, including Charles II of England. Robert Boyle [3] heard of this substance without being informed of its mode of preparation, other than that it was obtained from an animal source. On October 14, 1680, he deposited a sealed packet with the Secretary of the Royal Society. This included a paper containing an account of the preparation of phosphorus from urine; it was published posthumously in 1693. Robert Boyle said:

> On September 30, 1680, there was taken a considerable quantity of man's urine (because the liquor yields but a small proportion of the desired quintessence), and of this a good part at least had been for a pretty while digested before it was used. Then this liquor was distilled with a moderate heat, till the spirituous and saline parts were drawn off, after which the superfluous moisture also was abstracted (or evaporated away), till the remaining substance was brought to the consistence of a somewhat thick syrup, or a thin extract. This done, it was well incorporated with thrice its weight of fine white sand, and the mixture being put into a strong stone retort, to which a large receiver (in good part filled with water) was so joyn'd that the nose of the retort did almost touch the water. Then, the two vessels being carefully luted together, a naked fire was gradually administered for five or six hours, that of that which was either phlegmatick or volatile might come over first. When this was done the fire was encreased, and at length for five or six hours was made as strong and intense as the furnace (which was not bad) was capable of giving (which violence of fire is a circumstance not to be omitted in the operation). By this means there came over good store of white fumes, almost like those that appear in the distillation of oyl of vitriol; and when those fumes are passed and the receiver grew clear, they were after a while succeeded by another sort, that seemed in the receiver to give a faint, blewish light, almost like that of little burning matches dipped in sulphur. And, last of all, the fire being very vehement, there passed over another substance that was judg'd more ponderous than the former, because it fell through the water to the bottom of the receiver, whence being taken out (and partly even whilst it stay'd there), it appeared by several effects and other phenomena to be such a kind of substance as we desired and expected.

According to G. W. Stahl, J. D. Kraft alleged that he communicated to R. Boyle the mode of preparing phosphorus during his visit to England, but this assertion is generally discredited. F. Hoefer summed up his opinion:

> Comme il est le premier qui ait fait connaitre publiquement la préparation de ce corps, à l'aide d'un procéde que personne ne lui avait appris, on pourrait, avec quelque justice, réclaimer pour lui l'honneur de la découverte du phosphore.

According to F. Hoefer, a manuscript entitled *Ordinatio Alchid Bechil Saraceni philosophi*—contained in the collection of alchemical manuscripts at the Bibliothèque Royal, Paris—shows that about the twelfth century Alchid Bechil obtained what he called *escarboucle* by distilling urine with clay, lime, and carbonaceous matters, and that it is highly probable that phosphorus was known as *un très-grand secret* to the Arabian alchemists. They seem to have been continually distilling all kinds of phosphatic materials—urine, bones, etc.—under conditions where phosphorus is sure to have been produced.

According to J. Bell, and G. Gore:

> In London, about the beginning of the eighteenth century, R. Boyle's assistant, A. G. Hanckewitz made phosphorus by R. Boyle's process and sold it in Europe The demand seemed in part due, as A. G. Hanckewitz expressed it, "to the alchemists who work on microcosmical substances, and out of it they promise themselves golden mountains." A. G. Hanckewitz had the monopoly of its sale for many years, so that it was sometimes called *English*, or *Boyle's phosphorus*; as well as *Kunckel's phosphorus*, *Brand's phosphorus*, and *Kraft's phosphorus*. To distinguish this new phosphorus from the phosphorescent minerals, J. von Kunckel called it *phosphorus mirabilis*, and *lumen constans*; R. Boyle designated it *noctiluca consistens*, *noctiluca gummosa*, *noctiluca constans*, *noctiluca aërea*, and *noctiluca glacialis*; while others also called it *phosphorus fulgurans*, *phosphorus igneus*, *phosphorus pyropus*, etc.

According to H. Peters,[4] there is a letter from J. G. Gmelin of Tübingen to J. W. Dieterich of Nürnberg, in the possession of H. Kämmerer, which shows that J. G. Gmelin described the preparation of phosphorus from urine and charcoal in Sweden in 1715. In 1737, the secret was learned in France, and a description of the process of manufacture, namely, by distilling urine with sand and carbon, was described by J. Hellot. A. S. Marggraf appears to have obtained better yields by using lead chloride in place of sand. In 1781, J. R. Spielmann described the preparation of phosphoric acid from urine. The history of phosphorus was discussed by L. Franck, H. Peters, and L. P. J. Palet. B. Albinus detected phosphorus in mustard and cress; and A. S. Marggraf, in the growths from mustard, cress, wheat, etc. In 1780, J. G. Gahn found a mineral in which the phosphorus was united with lead. T. Bergman, and J. L. Proust found phosphorus in apatite.

In 1771, C. W. Scheele mentioned the occurrence of phosphorus in bones, while T. Bergman said that the fact was discovered by J. G. Gahn, about 1770.

There is some doubt as to the discoverer of the phosphorus compounds in bones. Neither C. W. Scheele[5] nor J. G. Gahn published a special paper on the subject. In his paper: *Undersökning om fluss-spat och dess syra* (1771), C. W. Scheele said that "it has recently been discovered that the earth of bones or horns is calcarious earth combined with phosphoric acid." T. Bergman, in his edition of H. T. Scheffer's *Chemische Vorlesungen* (Greisswald, 1779), ascribed the discovery of phosphorus in bones to J. G. Gahn in 1769. A. E. Nordenskjöld, from one of C. W. Scheele's letters dated Frühjahr, 1770, inferred that J. G. Gahn and C. W. Scheele made the discovery together in the summer of 1770. H. Gahn, brother of J. G. Gahn, said that the discovery was made by J. G. Gahn and confirmed by C. W. Scheele.

G. Homberg[6] considered phosphorus to consist of phlogiston united with an acid so that during combustion the phlogiston escaped, and the acid remained as a residue. G. W. Stahl, and J. Hellot supposed the acidic constituent to be hydrochloric acid; F. Hoffmann, a compound of sulphuric and hydrochloric acids; H. Boerhaave, sulphuric acid; and A. G. Hanckewitz, sulphur. A. S. Marggraf showed that G. W. Stahl's hypothesis is very improbable, and that in the conversion of phosphorus to phosphoric acid (*q.v.*) there is an increase in weight. A. L. Lavoisier's investigations on combustion demonstrated the elementary nature of phosphorus; so that later suggestions of the complexity of phosphorus are mere speculations.

C. Girtanner's fanciful suggestion that phosphorus contains much hydrogen and a little oxygen, was disproved by H. Davy, who observed the formation of neither oxygen nor hydrogen chloride during the combustion of phosphorus in chlorine. H. Davy, however, did find so much hydrogen was given off from phosphorus during the passage of the electric current that he could say "the hydrogen cannot well be considered as an accidental ingredient of this body." J. N. Lockyer also assumed that phosphorus was a compound of hydrogen, but nothing new developed from the hypothesis. F. B. Fittica alleged that by heating phosphorus with ammonium nitrate it can be transformed into arsenic; that arsenic, in turn, is a compound of nitrogen, phosphorus, and oxygen, PN_2O; and that red phosphorus is a sulphide, N_2SH_2. C. Winkler, A. C. Christomanos, G. R. Gyzander, and M. C. Schuyten obtained no support for F. B. Fittica's sterile suggestion. Any arsenic in the final product of his experiment must have been present as impurity in the initial materials.

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§ 2. The Occurrence of Phosphorus

> Phosphorus is nearly the most widely and evenly distributed element on the surface of the earth, and probably the most subdivided. This can be readily understood when the important part which phosphoric acid plays and has played in the vital cosmos is taken into consideration. Phosphorus was on the earth in gaseous, liquid, or solid form before the dawn of life, and since then, all animal and vegetable creations have combined with the physical forces always at work in inanimate nature to distribute and redistribute the phosphorus, to divide it up, and carry it from place to place. If the biography of atoms could be written, the chapters on phosphorus would be the most interesting and the most varied.—W. B. M. DAVIDSON (1893).

Phosphorus has not been found to occur in a free state on the earth. If it were formed by a natural process, the affinity of phosphorus for oxygen would result in the oxidization of the element where accessible to atm. air. Phosphorus is fairly abundantly distributed and, with a few minor exceptions, it occurs in the mineral kingdom as a phosphate. Thus, nearly all igneous rocks contain a little phosphate generally as apatite. According to F. W. Clarke and H. S. Washington's estimate,[1] it is more abundant than carbon, and less abundant than chlorine in the ten-mile crust of the earth, hydrosphere, and atmosphere. Phosphorus is 12th in the list of the elements which make up 99·6 per cent. of the crust of the earth. The numbers are: oxygen, 49·19 per cent.; iron, 4·68; chlorine, 0·228; phosphorus, 0·142; and carbon, 0·139. It is 10th in the list for igneous and sedimentary rocks, and also for igneous rocks. The average percentage of P_2O_5 in igneous rocks is 0·13; in shale, 0·17; in sedimentary rocks, 0·09; in sandstone, 0·08; and in limestone, 0·04. J. H. L. Vogt estimated that the igneous rocks contain 0·22 per cent. of phosphorus. This subject was discussed by H. S. Washington, V. M. Goldschmidt, W. D. Harkins, J. F. Kemp, W. Lindgren, W. Vernadsky, and G. Tammann. W. Vernadsky gave 0·056 for the percentage amount, and 0·1 for the atomic proportion. V. M. Goldschmidt estimated that the natural supplies of available phosphorus will last over a century, but M. Pietrkowsky pointed out that the estimate does not include the North African deposits. The subject was discussed by W. Packard.

H. A. Rowland,[2] and M. N. Saha could find no evidence in the solar spectrum of the existence of phosphorus in the sun; but phosphorus of extra-terrestrial origin has been found in meteorites. O. C. Farrington reported the occurrence of free phosphorus in the meteorite which fell in Saline Township. Iron phosphide, and iron nickel phosphide have been found in numerous meteorites [3]—*vide infra*, iron phosphide, and schreibersite, and rhabdite.

The salts of phosphoric acid are very widely distributed; and, as J. B. J. D. Boussingault [4] noticed, most of the naturally occurring phosphates are salts of orthophosphoric acid. This, however, does not necessarily mean that they were not formed at a high temp. W. B. Phillips has compiled a list of 141 minerals with the equivalent of over one per cent. of phosphoric acid. In the appended list, the formulæ are more or less variable and have not always the same significance as the formulæ of chemical compounds.

Amblygonite, $Al(Li,F,OH)PO_4$, a mixture of phosphate of aluminium and fluoride of lithium and sodium, with sometimes a little potassium (triclinic) ; *apatite* $(F,Cl)Ca_5(PO_4)_3$, normal calcium phosphate (hexagonal) ; *augelite*, $Al_2(OH)_3PO_4$, hydrated phosphate of aluminium, containing also a little calcium, iron, and manganese (monoclinic) ; *autunite*, $(UrO_2)_2Ca(PO_4)_2.8H_2O$, hydrated phosphate of uranium and calcium, containing also sometimes a little barium, manganese, magnesium, and possibly tin (rhombic) ; *barrandite* $(Al,Fe)PO_4.2H_2O$, hydrated phosphate of iron and aluminium (massive) ; *beraunite*, $Fe_5(OH)_6(PO_4)_3.3H_2O$, hydrated phosphate of iron (monoclinic) ; *beryllonite*, $BeNaPO_4$; *bobierrite*, $Mg_3(PO_4)_2.8H_2O$, normal phosphate of magnesium with water (monoclinic) ; *borickite*, $Fe_4(OH)_6Ca(PO_4)_2.3H_2O$, hydrated phosphate of iron and calcium, with sometimes a little magnesium (massive) ; *brushite*, $CaHPO_4.2H_2O$, hydrated monobasic calcium phosphate (monoclinic) ; *callaite*, $Al_2(OH)_3PO_4.6H_2O$ (rhombic) ; *calcioferrite*, $(Fe,Al)_3(OH)_3(Ca,Mg)_3(PO_4)_4.8H_2O$; hydrated phosphate of iron and calcium, containing also aluminium and magnesium (possibly monoclinic) ; *callainite*, $AlPO_4.2\frac{1}{2}H_2O$, hydrated phosphate of aluminium with a little silica, iron, and calcium (massive) ; *chalcosiderite*, $(AlFe)_2(FeO)_4Cu(PO_4)_4.8H_2O$, hydrated phosphate of iron with aluminium and copper (triclinic) ; *childrenite*, $Al(OH)_2(Fe_3Mn_3Ca)PO_4.H_2O$, hydrated phosphate of iron and aluminium, with manganese, and a little magnesium and calcium (rhombic) ; *cirrolite*, $Ca_3Al_2(OH)_3(PO_4)_3$, hydrated phosphate of calcium and aluminium with a little silica, manganese, iron, magnesium, and lead (massive) ; *collophane*, $Ca_3(PO_4)_2.H_2O$; *dahllite*, $Ca_7PO_4(CO_3).\frac{1}{2}H_2O$; *delvauxite*, $Fe_4(OH)_6(PO_4)_2.17H_2O$, variety arseniosiderite, hydrated phosphate of iron, and calcium (?) ; *diadochite*, $Fe_4O(OH)_2(HSO_4)_2(PO_4)_2$, hydrated sulphate and phosphate of iron (possibly monoclinic) ; *dihydrite*, $Cu(CuOH)_4(PO_4)_2$, hydrated phosphate of copper (triclinic) ; *chlite*, $Cu(CuOH)_4(PO_4)_2.H_2O$, hydrated phosphate of copper, with vanadium (rhombic) ; *eleonorite*, $(FeOH)_3(PO_4)_2.2\frac{1}{2}H_2O$, hydrated phosphate of iron (monoclinic) ; *eosphorite*, $Al(OH)_2(Mn,Fe)PO_4.H_2O$, hydrated phosphate of manganese, aluminium, and iron, with a little calcium and sodium (rhombic) ; *evansite*, $Al_3(OH)_6PO_4.6H_2O$, hydrated phosphate of aluminium (massive) ; *fairfieldite*, $(Ca,Mn,Fe)(PO_4)_2.2H_2O$, hydrated normal phosphate of calcium, with manganese and iron (triclinic) ; *fillowite*, $(Ca,Na_2,Fe,Mn)_3(PO_4)_2.\frac{1}{3}H_2O$, normal phosphate of manganese, iron, calcium, and sodium, with a little water (monoclinic) ; *fischerite*, $Al_2(OH)_3PO_4.6H_2O$, hydrated phosphate of aluminium, with a little iron, copper, and manganese (rhombic) ; *gibbsite*, $AlPO_4.4H_2O$; *hamlinite*, $3Al(OH)_2(SrOH)P_2O_7$; *hannayite*, $Mg_3(NH_4)_2H_4(PO_4)_4.8H_2O$, hydrated phosphate of ammonium and magnesium (triclinic) ; *henwoodite*, $CuAl_4,H_{10}(PO_4)_8 6H_2O$, hydrated phosphate of aluminium, containing copper (massive) ; *herderite*, $CaBe(OH,F)PO_4$, a mixture of phosphate and fluoride of calcium and beryllium, sometimes containing aluminium (rhombic) ; *hopeite*, $Zn_3(PO_4)_2.4H_2O$, hydrated phosphate of zinc, with a little cadmium (rhombic) ; *hureaulite* $(MnFe)_5H_2(PO_4)_4.4H_2O$, hydrated phosphate of manganese, and iron, with a little silica (monoclinic) ; *isoclase*, $Ca_2(OH)PO_4.2H_2O$, hydrated normal phosphate of calcium, with calcium hydrate ; contains, also, magnesium, sodium, and a little iron and aluminium (monoclinic) ; *kakoxene*, $Fe_2(OH)_3PO_4.4\frac{1}{2}H_2O$; *kraurite*, $Fe_2(OH)_3PO_4$ (rhombic) ; *laxmannite*, $(Pb,Cu)_3(PO_4)_2\text{-}Pb\{Pb_2O(CrO_4)_2\}$, a mixture of chromate and phosphate of lead and copper, with a little iron and water (monoclinic) ; *lazulite*, $(HOAl)_2.Mg(Fe,Ca)(PO_4)_2$, hydrated phosphate of aluminium, magnesium, and iron, sometimes containing a little calcium, manganese, silica, and copper (monoclinic) ; *libethenite*, $CuPO_4.CuOH$, hydrated phosphate of copper, with sometimes a little arsenic and iron (rhombic) ; *ludlamite*, $Fe_5(FeOH)_2(PO_4)_4.8H_2O$, hydrated phosphate of iron (monoclinic) ; *lüneburgite*, $Mg(BO_2)_2.2MgHPO_4.7H_2O$, a mixture of hydrated phosphate and borate of magnesium, with a little fluorine (hexagonal) ; *martinite*, $Ca_5H_2(PO_4)_4.\frac{1}{2}H_2O$; *messelite*, $(Ca,Fe,Mg)_3(PO_4)_2.2\frac{1}{2}H_2O$; *minervite*, $AlPO_4.3\frac{1}{2}H_2O$; *monazite*, $CePO_4$, with lanthanum and thorium (monoclinic) ; *monetite*, $CaHPO_4$, monobasic phosphate of calcium (triclinic) ; *natrophyllite*, $Na(Mn,Fe)PO_4$ (rhombic) ; *newberyite*, $MgHPO_4.3H_2O$, hydrated monobasic phosphate of magnesium (rhombic) ; *peganite*, $Al_2(OH)_3PO_4.1\frac{1}{2}H_2O$, hydrated phosphate of aluminium, with a little copper and iron (rhombic) ; *phosphorochalcite*, $Cu(OH)_3PO_4$; *phosphuranylite*, hydrous phosphate of uranium, with lead (massive) ; *polysphaerite* $(CaPbH)_5F(PO_4)_3$, variety of pyromorphite, containing 11 per cent. phosphate of calcium (massive) ; *pseudolibethenite*, $Cu(CuOH)PO_4.\frac{1}{2}H_2O$, variety of libethenite, but contains twice as much water (hexagonal or rhombic) ; *pyromorphite*, $CaPb_5(PO_4)_3$, a mixture of phosphate and chloride of lead, containing, also, sometimes aluminium, arsenic, calcium, iron, chromium, and silica (hexagonal) ; *reddingite* $(Mn,Fe)_3(PO_4)_2.3H_2O$, hydrated phosphate of manganese, sometimes containing iron (rhombic) ; *sphaerite*, $Al_5(OH)_9(PO_4)_2.12H_2O$, hydrated phosphate of aluminium, with a little magnesium, calcium, and silica (massive) ; *staffelite*, $Ca_0(PO_4)(CO_3)(CaF_2)_2.H_2O$, alteration product of apatite, contains calcium, iron, fluorine, carbonic acid, aluminium, water, and iodine (hexagonal) ; *stercorite*, $NaH(NH_4)PO_4.4H_2O$, hydrated phosphate of sodium and ammonium with sodium chloride, calcium carbonate, calcium phosphate, magnesium, etc. (monoclinic) ; *svanbergite*,

$Na_3(CaOH)(AlO)_6(SO_4)_2(PO_4)_2.3H_2O$, hydrated phosphate and sulphate of aluminium and sodium, with calcium and iron, and sometimes a little lead and magnesium (hexagonal); *tagilite*, $Cu(CuOH)PO_4.H_2O$, hydrated phosphate of copper, with sometimes a little iron (monoclinic); *tavistockite*, $Ca_3Al_2(OH)_6(PO_4)_2.8H_2O$, hydrated phosphate of calcium and aluminium (massive); *triphyline* $(Mn,Li,Fe)(PO_4)$, phosphate of iron, manganese, and lithium, with a little sodium, calcium, magnesium, potassium, silica, and water (rhombic); *triplite*, $F(Mn,Fe)_2PO_4$, phosphate of iron and manganese, sometimes with a little calcium, magnesium, sodium, fluorine, water, silica, and lithium (monoclinic ?); *triploidite*, $(Fe,Mn)(FeHO,Mn)PO_4$, phosphate of manganese and iron, with a little water and calcium (monoclinic); *trolleite*, $Al_4(OH)_3(PO_4)_3$, hydrated phosphate of aluminium, and a little iron and calcium (massive); *uranocircite* $(UO_2)_2Ba(PO_4)_2.8H_2O$, hydrated phosphate of uranium and barium (rhombic); *variscite*, $AlPO_4.2H_2O$, hydrated phosphate of aluminium, (rhombic); *vivianite*, $Fe_3(PO_4)_2.8H_2O$, hydrated phosphate of iron, sometimes with a little aluminium, manganese, silica, and organic matter; consists essentially of water and ferrous and ferric phosphate (monoclinic); *wagnerite*, FMg_2PO_4, normal phosphate of magnesium, with fluorine, iron and calcium, and sometimes a little manganese and aluminium (monoclinic); *wavellite* $(AlOH)_3(PO_4)_2.5H_2O$, hydrated phosphate of aluminium, sometimes a little iron, fluorine, silica, calcium, and manganese (rhombic); *xenotime*, YPO_4, phosphate of yttrium, sometimes, also, with cerium; lanthanum, didymium, uranium, titanium, zirconium, fluorine, iron, and silica (tetragonal); *zepharovichite*, $AlPO_4.3H_2O$, hydrated phosphate of aluminium, with silica and calcium (massive).

Deposits of phosphate rock occur in most countries; they are found in the marine beds ranging from the old Cambrian beds to the Tertiary beds, and in the oceans of to-day, dredgings show that such deposits are being formed. According to F. W. Clarke,[5] the phosphatic concretions found on the ocean floor consist mainly of calcium phosphate and carbonate mixed with sand and clay. They have been discussed by L. W. Collet, L. Cayeux, etc. According to J. Murray and A. F. Renard, they are derived from the decaying bones of dead animals upon which carbonic acid exerts a powerful solvent action. They form round various nuclei—principally shells. In many cases, the phosphatic matter was first deposited in the cavities of shells, around which the nodules continued to grow. The ammoniacal matters from the decomposing organic matter in bone probably played some part in the precipitation of the calcium phosphate. Lime is the predominant base in the natural phosphates which have an economic value, and such are often called *phosphorite* (*q.v.*). Analyses were reported by T. Steel, etc. The composition of a few samples is indicated in Table I. There is usually in addition some silica, organic matter, and chlorine. Iodine has been repeatedly detected in phosphorites, but the evidence with respect to bromine is not so clear. The first analysis is by G. Steiger[6]; the second by G. H. Eldridge; and the third by O. Tietze. Phosphate rock is often mined by steam shovels, and usually prepared for the market by a preliminary screening and washing to remove clay; it is then crushed, screened, and picked to a grade 65–80 per cent. normal calcium phosphate.

TABLE I.—COMPOSITION OF SOME NATURAL PHOSPHATES.

	Crawford Mts., Utah.	Land pebbles of Florida.	Gafsa, Tunis.	Acuba, West Indies.	Ain Dibha, Algiers.
Insoluble . . .	1·82	6·69	3·05	—	—
Almina, Al_2O_3 . .	0·50	2·14	1·09	2·95	1·93
Ferric oxide, Fe_2O_3 . .	0·26	0·61	0·64	1·80	
Magnesia, MgO . .	0·22	0·33	0·57	—	0·48
Lime, CaO . . .	50·97	46·03	48·58	46·37	50·71
Alkali, $(K,Na)_2O$ . .	2·47	—	0·09	—	—
Water, H_2O . . .	1·05	4·26	—	0·62	—
Carbon dioxide, CO_2 .	1·72	3·93	4·60	1·53	6·15
Phosphoric oxide, P_2O_5 .	36·35	31·50	29·74	35·70	32·22
Sulphuric oxide, SO_3 .	2·98	—	2·75	1·55	1·54
Fluorine, F . . .	0·40	1·86	2·12	4·22	2·80

The guanos have undergone more or less decomposition by the action of rain, etc., and they are sold on the " per cent. of nitrogen " they contain. Some guanos are enriched by the addition of dried blood, ammonium phosphate, etc., and sold as special fertilizers. Nitrogenous matters and potash, all valuable manures, are also associated with guano. The animal skeleton is mainly composed of bone. Bones contain non-combustible mineral matters, and combustible organic matters. Fatty organic matter can be extracted by digesting the bones with solvents like benzene, carbon disulphide, ether, chloroform, etc., which dissolve the fat, and leave behind *degreased bones ;* the gelatinous matters—glue—can be extracted by digesting the bones with water heated under pressure—*degelatinized bones* remain behind. The degelatinized bones still contain combustible carbonaceous matters, and if they be heated in iron retorts, out of contact with air, gaseous and liquid products distil over, and a residue of *animal charcoal* remains in the retort. Dippel's bone oil occurs among the liquid products of the distillation. A similar result is obtained if degreased or raw bones be heated in the retorts. If animal charcoal, or degreased, degelatinized, or raw bones be heated in air, the organic matters burn, and *bone-ash* remains. The composition of bone-ash may be taken as

P_2O_5	CaO	MgO	Fe_2O_3 and Al_2O_3	SiO_2	CO_2	H_2O	Alkalies
39·5	52·5	1·0	0·2	0·5	0·9	1·8	1·4

with about 2 per cent. of organic matter. W. F. de Jong said that the X-radiograms of modern and fossilized bones show lines characteristic of the fluorapatite type of structure and nothing else. The fundamental mineral is probably $3Ca_3(PO_4)_2,CaCO_3$, in which the carbonate radical may be replaced, as in fossilization, by fluorine, chlorine, or sulphate, and perhaps by other radicals, whilst some of the calcium may be replaced by magnesium, and possibly also by iron and aluminium. The diffuse nature of the X-ray lines indicates that the crystals present contain only some tens or hundreds of mols, but on incineration the crystal size is increased. No evidence could be found of the existence in bones of the colloidal *collophanite*, $Ca_3P_2O_8.H_2O$, described by J. D. Dana. Bone-ash is used in the manufacture of manures, phosphorus, English porcelain, cupels, baking powder, etc.

The larger deposits of calcium phosphate or phosphorite are probably of marine origin. The traces of phosphates in sea-water are absorbed in the shell, bones, and tissue of marine organisms ; and the remains accumulate in the ooze at the bottom of the sea. The accompanying calcium carbonate is in part removed owing to its slight solubility ; some phosphate is at the same time dissolved and in part redeposited around fragments of shells or bones so as to form phosphatic nodules, common in phosphorite beds and on the ocean floor—*vide supra.* The deposits on the sea-bottom are further conc. when they are elevated into a land surface by the leaching away of calcium carbonate by subterranean water. The phosphorite deposits are not crystalline, but form compact or concretionary earthy masses. Some of the purer deposits approximate to apatite or fluorapatite, $Ca_5(PO_4)_3F$, in composition, but others approach normal calcium phosphate, $Ca_3(PO_4)_2$, in composition. A. Carnot says that the concretionary phosphates are deficient in fluorine, while in the sedimentary the fluorine approximates to the apatite ratio.

Large deposits of phosphorite are worked in the cretaceous beds of northern France ; while in south-western *France,* phosphates occur along with clay in irregular fissures in the Jurassic limestone. The French deposits are in Nord, Pas de Calais, Cambresis, Somme et Oise, Ardennes, Meuse, Marne, Yonne, Cote-d'or, Haute-Saône, Cher, Indre, Sarthe, Lot, Tarn-et-Garonne, Lot-et-Garonne, Gard, Ardêche, Drôme, Isère, Pyrenees, etc. The *German* deposits of phosphorite include those of Hessen-Nassau, Braunschweig, Leipzig, Vogtlandes, Amberg, Darmstadt, Ruhrrevier, etc. Deposits occur at Hesbaye, Hennegau, etc., in *Belgium ;* at Estremadura—Logrosan and Caceres—in *Spain ;* near Potalegre and Marvao in *Portugal.* The deposits in *Great Britain* are at Cwmgwnnen in the lower Silurian series of North Wales ; and in Bedfordshire, Cambridgeshire, Norfolk, Suffolk, Essex, etc. Phosphorite is found at Malta ; a zone extending from the Volga, near Simbirsk, into Desna (Smolensk) and into Grodno ; and in Podolia in *Russia ;* and in *Sweden.* There are also large deposits along the frontier of *Algeria* and *Tunis* in the lower Eocene beds over the Cretaceous strata. M. Pietrkowsky estimates that there are 1,000,000,000 tons of phosphates available in *Morocco,* and that there are also large deposits in *Egypt.* Deposits also occur in *Natal.* The deposits in the *United States* extend along the Atlantic coast belt of Tertiary rocks in North and South Carolina, Florida—Pennsylvania, and Alabama ; in Arkansas ; in the Silurian and Devonian strata of Tennessee ; and in the carboniferous beds of Utah, Wyoming, and Idaho. There is a phosphate bed in Montana. The deposits in Florida are the most productive. The phosphorites of Florida exist as *boulder or rock phosphate* found in ledges, and it contains as high as 80 per cent. normal calcium phosphate with 2·5 per cent. of iron oxide and alumina ; as *pebble rock*, found in mounds or beaches, and it contains about 62 per cent. of normal calcium phosphate, and 3 per cent. of iron oxide and alumina ; and *soft phosphate*, found in cavities or pockets, and it contains about 65 per cent. of normal calcium phosphate and 6 per cent. of iron oxide and alumina. Apatite occurs in the Laurentian limestone of North Elmsley and North Burgess, of Canada. Phosphorite deposits are found in the *West Indies*—Curaçao, Bonaire, Aruba, Leeward Isles, Redonda, Barbuda, St. Martin, Sombrero, Alta Vela, Navassa, Pedro Keys, and Avalo. In *Mexico* phosphorite occurs near Mazapil and Concepcion del Oro. They occur in Christmas Island in the Indian Ocean ; Noto, Bonin, Shimane, Hyuga, etc., in *Japan*; Ninh-Binh in *China ;* the islands of the coast of *Arabia ;* Palestine ; Bessarabia; etc. Phosphorite deposits occur near the coast in *Bolivia*, in *Chile*, and at Rata in *Brazil.* Phosphorite has also been found on the Ocean and Pleasant (Nauru) Islands, and the Islands of Huon, Baker, Howland, Jarvis, Malden, Starbuck, Enderbury, and Fanning; the *Polynesian* islands; Dandaraga in Western *Australia ;* in Otago, *New Zealand.* H. Laubmann and H. Steinmetz discussed the phosphatic rocks of Bavaria.

Thousands of analyses[7] reported in connection with agriculture show that fertile soils contain up to 0·5 per cent. of phosphoric acid—probably as aluminium or iron phosphates. All limestones, chalks, and dolomites contain small proportions, and this requires attention in the selection of limestone as a flux for smelting iron. The younger limestones were found by W. B. M. Davidson[8] to be usually the more phosphatic. G. Freda reported its presence in volcanic lava ; J. A. Barral, and A. Dupré, in rain-water ; and A. Voelcker, in boiler-scale. Analyses of the waters of the ocean show the presence of varying amounts of phosphoric acid—*e.g.* some parts of the Gulf-stream are said to be more phosphatic than the surrounding waters of the Atlantic. The presence of soluble phosphates has been reported in many springs, chiefly in limestone districts. D. J. Matthews found the amount of phosphoric acid in the sea-water off Plymouth reached a maximum—0·06 mgrm. P_2O_5 per litre—in December, 1915, and it decreased irregularly to a minimum—0·01 mgrm. per litre—in April-May, 1916 ; and again attained the same maximum as before about January, 1917. This seasonal variation is attributed to the removal of phosphates from soln. by algæ, diatoms, etc. The subject was studied by R. Gill, and W. R. G. Atkins.

As indicated in connection with the history of phosphorus, the presence of this element in the vegetable kingdom was recognized by B. Albinus,[9] and A. S. Marggraf near the middle of the seventcenth century ; and a few years afterwards by C. W. Scheele in bones. Numerous analysis of vegetable matters, plants, plant-ashes, and coal show that they probably contain phosphates. J. Davidson studied the changes in the phosphorus-content of wheat seedlings during germination and growth; and W. H. and C. B. Peterson, the phosphorus-content of cabbage. C. Palmer discussed the occurrence of phosphorus in petroleum. The presence of phosphorus in the animal kingdom has been established by numerous analyses of animal-tissue, bones,[10] blood,[11] brain, urine,[12] fæces,[13] etc., and in the eggs of fishes and birds, in oysters, in sponges, etc. Naturally therefore, phosphates occur in food-stuffs.[14]

The phosphorus cycle in nature.—Small quantities of phosphates are found in granite rocks. By the weathering and decay of these rocks, the combined phosphorus ultimately finds its way into the soil, spring-waters, and the sea. The geological *rôle* of phosphorus has been discussed by W. Lindgren,[15] and E. Blackwelder. The phosphates disseminated in rocks as apatite, or accumulated in iron ores, pegmatites, and veins, are to a large extent dissipated by weathering processes in the form of complex alkali calcium and iron phosphate soln., which eventually find their way to the sea. Part enters into the formation of new sediments as complex fluo-carbonato-phosphates. These sediments are folded and uplifted, and become dry-land. The surface waters concentrate part into deposits of economic importance, and dissipate part as soluble phosphates; or the sediments may become absorbed in rock magmas and re-form apatite. All fertile soils contain phosphorus, since phosphorus is needed to build up certain essential parts of the tissue of growing vegetation. Plants require phosphorus from their earliest life, and seeds contain a plentiful supply for the germination of the embryo. The equivalent of one pound of phosphorus is said to be present in about 100 lbs. of corn, and in about 1200 lbs. of fodder. Animals, too, like plants, must have phosphorus, and they are dependent for their supply upon the plants or upon the herbivorous animals upon which they feed. Animals concentrate the phosphorus in their bones and tissue. The bones of an adult man contain the equivalent of 1900 to 2400 grms. of normal calcium phosphate.

L. A. J. Quetelet's analysis of an average man weighing 154 lbs. is: Water, 116 lbs.; dry matter, 38 lbs. The 38 lbs. of dry matter consist of fat, 6 lbs.; flesh, skin, and blood, 18 lbs.; and bone, 14 lbs. The 14 lbs. of bone consist of gelatine, 4⅔ lbs., and 9⅓ mineral matter. The liquid blood contains water, 15⅔ lbs.; dry solid matter, 4⅓ lbs.; and this dry solid matter consists of fibrin, albumen, etc.; 4 lbs. fat, and a little sugar, ⅔ lb., and mineral matter, about ⅓ lb.

Dry bones, on the average, contain the equivalent of about 60 per cent. of tricalcium phosphate; teeth, 70 per cent.; crab and snail shells, 7 per cent. When the animals die, their remains help to build up phosphatic rocks. Thus, the story of the circulation of phosphorus is a cycle of processes involving the concentration and dissipation of that element. The waste of muscular and nervous tissue involves a decomposition of the phosphorus compounds. The products of decomposition are carried by the blood to the kidneys, and there excreted with the urine—chiefly as sodium ammonium phosphate. There seems to be a relation between the amount of phosphorus compounds discharged from the system, and the activity of the brain, and this led to the inference that phosphorus is a metabolic product of the activity of the brain, and that phosphate foods are needed for brain workers. The idea has crystallized in the well-worn phrase *ohne Phosphor kein Gedanke*—without phosphorus no thought. A similar statement might be made regarding several other elements. A normal adult excretes the equivalent of 3 to 4 grms. of phosphoric acid *per diem*. Part of this is derived from the food, and part from muscular waste. In this way, phosphorus finds its way back to the soil; or perhaps into the sewage, and finally into the sea. W. Lindgren thus describes the fate of the phosphorus which finds its way into the sea:

> In the sea-water the blue-green algæ concentrate phosphorus, certain molluscs, or crustaceans, feed on the algæ, and other meat-eating molluscs devour the vegetarians. Small fishes eat the molluscs, large fishes eat the small, finally seals and birds swallow the fishes, and so in about six transformations the phosphorus originally contained in the sea-water may come to rest in deposits of guano on desert islands or in accumulations of the bones of the vertebrate denizens of the sea.

Hence the origin of the phosphorus in the large deposits of guano—the excrement of sea-birds—on the islands off the Peruvian coast, and a number of islands in the South and the Caribbean Seas. Many islands have been stripped of the guano they once contained. The amount of phosphates returned from the sea as edible fish is insignificant in comparison with what is drained into the sea as sewage from towns. Processes for the recovery of the phosphates in sewage now attract attention, since that which escapes into the sea accumulates at the bottom, where it may be unproductive for countless ages before it is again able to take an active part in nature's great cycle of changes. The constant growth of crops by the farmer impoverishes the soil, and phosphatic manures are needed to make good the loss.

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§ 3. The Preparation of Phosphorus

The early workers on phosphorus prepared that element from urine which normally contains ammonium and sodium phosphates. Thus, R. Boyle[1] evaporated the urine to a syrupy consistency, and distilled the product either alone or admixed with sand or charcoal. The carbon produced by the decomposition of the organic matter in the urine, or added to it in the form of charcoal, decomposes the ammonium phosphate, without affecting the sodium phosphate. A. S. Marggraf mixed the conc. urine with lead chloride and charcoal powder, and heated the mass until it became pulverulent. The ammonium and sodium phosphates were converted into lead phosphate, and on distillation, the carbon liberated the phosphorus from the lead phosphate. G. A. Giobert mixed the unevaporated urine with lead nitrate or acetate ; washed the precipitated mixture of lead phosphate and sulphate ; mixed the precipitate with charcoal ; and distilled the dried product.

After J. G. Gahn[2] had shown in 1770 that phosphorus is an essential constituent of bone, C. W. Scheele obtained that element by dissolving the bone-ash in nitric acid, precipitating the lime with sulphuric acid, concentrating the clear soln. by evaporation, and distilling the product admixed with charcoal. J. M. J. Funke, B. Pelletier, T. Graham, M. Donovan, and P. F. Nicolas simplified the process by digesting the bone-ash directly with an excess of sulphuric acid, evaporating the clear filtrate containing calcium hydrophosphate, and distilling the dried product admixed with charcoal. A. F. de Fourcroy and L. N. Vauquelin mixed the soln. of calcium hydrophosphate with lead acetate, and collected the precipitated lead phosphate ; while J. J. Berzelius obtained his lead phosphate from the nitric acid soln. of bone-ash. In both cases, the lead phosphate was mixed with charcoal and distilled for phosphorus.

A. Nicolle decomposed the phosphate with nitric acid, and treated the soln. with potassium sulphate. The filtrate from the calcium sulphate was treated with mercurous nitrate ; and the mercury phosphate mixed with carbon and distilled—mercury was first obtained, then phosphorus. J. G. Gentele proposed to combine the manufacture of phosphorus with that of ammonium chloride by adding crude ammonium carbonate to soln. obtained by digesting the bones with hydrochloric acid. Phosphorus was obtained from the precipitated calcium phosphate, and ammonium chloride from the soln. R. Lammy also proposed extracting first ammonia then phosphorus by heating an intimate mixture of ammonium phosphate and carbon. W. M. C. Folie-Desjardins tried to manufacture phosphorus and an alkali silicate simultaneously. The phosphate was heated with an alkali sulphate or carbonate, with or without silica or flux. The aqueous extract contained the alkali phosphate. He then heated the alkali phosphate with silica and carbon—phosphorus was evolved, and the alkali silicate escaped. H. Fleck proposed to manufacture phosphorus and glue or gelatine by decomposing the de-greased bones with dil. hydrochloric acid to dissolve out the calcium phosphate, and leave the cartilaginous matter undissolved. The acid phosphate liquor was mixed with carbon, dried, and distilled for phosphorus. E. C. Mantrand decomposed an intimate mixture of calcium phosphate, carbon, and silica at a high temp. in an atm. of hydrogen chloride, or chlorine, when phosphorus, hydrogen phosphide, carbon dioxide, etc., are given off. J. H. Player mixed the phosphoric acid liquor with spent tan or finely powdered coal or coke ; carbonized the mixture to remove volatile organic matter ; and then distilled the residue in the usual way. B. W. Gerland proposed decomposing the bone-ash with sulphurous acid. A. Rossel heated phosphoric acid, or an alkali phosphate with zinc or aluminium ; at a low red-heat, the metal was dissolved and phosphorus set free. In the presence of silica, all the phosphorus can be driven off ; $6NaPO_3+10Al+3SiO_2=3Na_2SiO_3+5Al_2O_3+6P$; or $3Ca(PO_3)_2+10Al+3SiO_2=3CaSiO_3+5Al_2O_3+6P$. E. Minary and R. Soudry prepared phosphorus from a mixture of iron phosphate and coke ; and R. A. Brooman heated a mixture of silica, iron, coal, and calcium phosphate so as to form a fusible slag and iron phosphide. The latter when heated with sulphur, hydrogen sulphide, carbon disulphide, etc., furnished phosphorus. J. Townsend heated a mixture of aluminium phosphate (native) either along with carbon and a flux of common salt and borax, or with a mixture of potassium and sodium sulphates, and so obtained phosphorus. A. Shearer and R. R. Clapp heated aluminium phosphate mixed with carbon and sodium chloride in an atm. of hydrogen chloride: $2AlPO_4+4NaCl+3C+6HCl=2(AlCl_3.2NaCl)+3H_2+3CO+P_2O_5$; and at a white-heat: $P_2O_5+5C=2P+5CO$.

The manufacture of phosphorus from bone-ash offers many advantages, but bone-ash is perhaps the most expensive source of phosphorus, per unit. Natural phosphates containing at least 70 per cent. of normal calcium phosphate can be worked economically by the distillation process.

The bone-ash is first treated with sulphuric acid, sp. gr. 1·5, with constant agitation in a large wooden tun. Enough sulphuric acid is used to convert the whole of the calcium phosphate into phosphoric acid: $Ca_3(PO_4)_2+3H_2SO_4=3CaSO_4+2H_3PO_4$. In some modifications, sufficient acid is added for the reaction: $Ca_3(PO_4)_2+2H_2SO_4=2CaSO_4+CaH_4(PO_4)_2$. When the reaction is completed, the calcium sulphate is filtered off, and washed until the filtrate has a sp. gr. of about 1·010. The first fraction of the filtrate is reserved for concentration, while that with a sp. gr. below 1·050 is employed partly as the first washing liquor and partly for the decomposition of a further lot of phosphate. The liquor is conc. by evaporation in shallow pans heated with high-press. steam, or by steam-coils. The liquor is agitated during the evaporation. Most of the calcium sulphate held in soln. is deposited during the evaporation. The conc. acid of sp. gr. 1·325 to 1·500 is cooled in lead-lined store-tanks.

The conc. phosphoric acid is mixed with coarsely ground wood-charcoal, coke, or sawdust, and dried and charred in a cast-iron pot or muffle-furnace. The charred mixture is then added to bottle-shaped retorts made from fireclay. The furnace employed is analogous to that employed in the distillation of zinc. A double tier of the phosphorus retorts is arranged back to back, with their necks slightly protruding from the furnace. The necks of the retorts are luted to the furnace so as to prevent the access of air to the interior of the furnace. The temp. of the furnace is then raised to bright redness, and the retorts charged with the mixture by means of long-handled scoops. There are several types of condenser: in one form cast-iron pipes are luted to the retorts and the free end dips an inch or two into water contained in a trough fitted with a lid through which pipes leading from the retorts pass by means of luted faucets. The bottoms of the trough is inclined, so that the water is deeper at one end than at the other. The water in the trough soon gets warm, and the melted phosphorus collects at the deeper end of the trough. The temp. of the retorts is gradually raised to whiteness; the distillation occupies about 16 hrs. The crude phosphorus is then ready for purification.

In the retort, the phosphoric acid is converted into metaphosphoric acid at a red-heat, and at a higher temp., this acid is reduced by the carbon $2HPO_3+5C=2P+H_2O+5CO$. According to M. Neumann,[3] the reduction commences between 650° and 850°; and W. Hempel said that between 300° and 600°, any sulphuric acid which is present is decomposed, forming sulphur dioxide; the gases which come off at about 700° are combustible; and traces of phosphorus appear in the escaping gases at about 740°; most of the phosphorus distils over above 1050°, and the distillation is ended at about 1170°. At first, a mixture of carbon dioxide and monoxide and hydrogen escapes, and later the escaping gas is almost wholly carbon monoxide. According to T. Graham, some hydrogen phosphide will be found in the escaping gases, and this the more, the greater the proportion of water present in the mixture in the retort. J. Javal said that phosphoric acid is not so well adapted for the reduction as calcium phosphate because part volatilizes undecomposed, and T. Graham because the phosphoric acid, owing to the water which is present, yields a greater quantity of hydrogen phosphide. These objections do not weigh so much now as formerly, since the different stages of the process are more under control. When the bone-ash is converted into the hydrophosphate, the preliminary heating converts it into the metaphosphate: $CaH_4(PO_4)_2=Ca(PO_3)_2+2H_2O$; and the metaphosphate reacts with carbon in the retort: $3Ca(PO_3)_2+10C=4P+Ca_3(PO_4)_2+10CO$. To avoid the loss of one-third the phosphorus by its reversion to the normal phosphate, sand is admixed with the charge in the retort, when $2Ca(PO_3)_2+2SiO_2+10C=4P+2CaSiO_3+10CO$. The manufacture of phosphorus by these methods is discussed by J. L. Smith, W. Jettel, G. W. Stose, E. Orloff, J. B. Readman, etc. Electrical heating has now virtually displaced the retort processes.

F. Wöhler proposed heating to whiteness a mixture of bone-black with fine quartz-sand to obtain phosphorus; the affinity of the silica for the lime was said to facilitate the reducing action of the charcoal. Modifications were devised by E. Aubertin and L. Boblique, E. C. Mantrand, J. P. Serve, C. Brisson, etc. B. Moore, and J. W. Mellor showed that silica begins to react with the calcium phosphate at about 1200°, and that the reaction is favoured by the presence of carbon.

J. B. Readman showed that silica, intimately mixed with carbon and normal calcium phosphate, can, at a high temp., expel all the phosphorus, and form a fusible calcareous slag. Similar results were obtained with other phosphates—*e.g.* aluminium phosphate. The phosphorus can thus be obtained directly from raw phosphates without the employment of sulphuric acid at an intermediate stage in the process. Retorts were found to be unsuitable as a refractory; and shaft furnaces were not successful in working. J. B. Readman then tried to heat the mixture by passing an electric current through the raw materials contained in a closed furnace. T. Parker and A. E. Robinson patented an analogous process for producing phosphorus direct from the raw materials by electrically heating the phosphorus-bearing mixture inside the furnace, and not as in retort-distillation, outside the furnace. The idea is illustrated diagrammatically by Fig. 1.

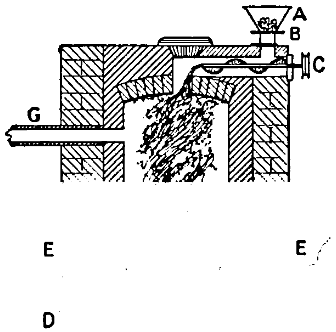

FIG. 1.—Electrical Furnace for the Manufacture of Phosphorus.

The mixture is heated in an electrical furnace fitted with carbon rods for conducting the electric current as illustrated in Fig. 1. Liquid slag is periodically tapped, and run from the bottom of the furnace *D*; and a new charge introduced so that the process is continuous. The charge is fed into the hopper *A*, and then passed into the chamber *B*, and to the conveyor *C*, which works something like an Archimedean screw, and carries the charge to the furnace. At the beginning of the operation an alternating current is sent through a pair of thin carbon "electrodes," not shown in the diagram, until the furnace is hot. When heated, the resistance of the furnace is reduced, and a current is sent through the electrodes *E*, and the thin electrodes are withdrawn. The phosphorus vapours and gases escape through a tube *G*. The electric current does its work by raising the temp. of the mass, not by electrolysis.

According to W. Hempel, and R. Müller, the reaction commences at about 1150°, when phosphorus vapour and carbon monoxide are evolved; the reaction is completed at about 1450°. The chemistry of the process is somewhat as follows: When calcium phosphate is heated with finely divided silica, SiO_2, calcium silicate, $CaSiO_3$, and phosphoric oxide are produced: $Ca_3(PO_4)_2+3SiO_2=3CaSiO_3+P_2O_5$. The latter is reduced by the carbon: $P_2O_5+5C=5CO+2P$. The carbon probably accelerates the rate of decomposition of the phosphate by the silica because the reaction progresses more quickly at a lower temp. in the presence of carbon than when carbon is absent. The composition of the slag is of importance, for the slag must be fluid enough to enable it to be run periodically from the furnace. This is determined by the mixture employed for charging the furnace. Most if not all the world's supply of phosphorus is obtained by the electrical process. Several modifications in the furnaces have been devised—by C. K. Harding, W. T. Gibbs, H. A. Irvine, T. Parker, R. K. Duncan, G. C. Landis, etc. H. Hilbert and A. Frank patented a process for phosphorus by heating a mixture of calcium phosphate and carbon in an electric furnace. Calcium carbide, CaC_2, is then the by-product: $Ca_3(PO_4)_2+14C=3CaC_2+8CO+2P$. The carbide is not pure enough for making acetylene, but is used for the preparation of calcium cyanamide. F. Tharaldsen used ferrosilicon or silicon carbide as the reducing agent; and A. E. V. Zealley discussed triplite as a source of phosphorus. C. S. Bradley and C. B. Jacobs used phosphates and phosphides of other metals than calcium in a similar manner.

The subject has been discussed by G. W. Stose, C. Herrmann, J. C. Chorley, etc. According to J. W. Richards, the furnaces at Niagara consume 11·6 kilowatts per hour per kilogram of phosphorus.

L. Dill electrolyzed a mixture of phosphoric acid of sp. gr. 1·7 to 1·9 and carbon in a closed vessel provided with a suitable opening, for the escape of phosphorus, etc. Carbon electrodes were used. The Electric Reduction Co., and F. J. Machalske proposed an analogous process.

If phosphorus vapour be condensed in cold water, the product resembles the raspings of cork and floats on water. The phosphorus from the condensers varies from a pale buff to brick-red, chocolate, or black colour. The variation in colour is mainly due to impurities, as well as the presence of the lower oxides, and of red phosphorus. The contamination of phosphorus by arsenic through the use of sulphuric acid contaminated with arsenic was observed by C. F. Bärwald,[4] C. Wittstock, F. P. Dulk, H. W. F. Wackenroder, E. Noelting and W. Feuerstein, G. Denigès, E. Merck, and J. von Liebig. According to P. I. Bonz, some samples of phosphorus which are yellow when fused, turn black when suddenly cooled—he said that boiling in alcohol destroys, while fusion with phosphoric acid develops, this property. Crude phosphorus mixed with fragments of sand, clay, and flue-dust can be cleaned by melting it under hot water, and agitating it with a wooden rake to allow the impurities to rise to the surface. When the phosphorus has solidified, the impurities can be collected, and redistilled, if necessary, to recover the phosphorus. The phosphorus can also be pressed through chamois-leather under hot water. The phosphorus can also be redistilled from an iron retort; or it can be agitated for a couple of hours with a warm mixture of sulphuric acid and potassium or sodium dichromate, as recommended by F. Wöhler, and A. Michaelis and M. Pitsch. The phosphorus has been purified by warming it with agitation in dil. nitric acid, or chlorine-water; by warming it in potash-lye or aq. ammonia, and then in water; by warming it in a soln. of potassium hydroxide in 75 per cent. alcohol as recommended by R. Böttger; and by dissolving it in carbon disulphide, and precipitating by potash-lye as recommended by R. Böttger. E. Noelting and W. Feuerstein freed phosphorus from arsenic, by distillation in steam. The purification of phosphorus for special purposes by distillation in a stream of hydrogen or other inert gas has been recommended by I. Remsen and E. H. Keiser, J. Böeseken, and A. Stock. A. Smits and H. L. de Leeuw purified the element by distillation and fractional crystallization in a highly exhausted atm., and obtained a colourless crystalline product. The phosphorus melted under hot water can be readily moulded into any desired shape, and it is commonly moulded into sticks. K. Seubert has devised a mould for this purpose. It is preserved in darkness under water, or under a non-freezing liquid like alcohol and water, or glycerol.

If the fused element be shaken up with a warm liquid until cold, it furnishes the so-called **granulated phosphorus**. J. L. Casaseca recommended alcohol of sp. gr. 0·85 in preference to water; R. Böttger, human urine, or an aq. soln. of urea; N. Blondlot, soln. of various salts, or sugar; and H. Schiff, methyl alcohol, actone, aq. ammonia, soln. of gum, dextrine, glue, starch, ammonium carbonate, etc.

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§ 4. The Allotropic Forms of Phosphorus

L. Wolf and K. Ristau [1] observed that *colourless phosphorus* can be obtained pure only in a darkened room in the absence of oxygen and moisture. It is best obtained in an atm. of nitrogen either by fractional distillation, or by fractional crystallization. It is either a colourless, transparent, glassy mass, or it is white and finely crystalline. It melts to a clear, colourless liquid. It is stable under the abovenamed conditions, but rapidly becomes yellow in light.

The early workers—H. A. von Vogel, C. W. Böckmann, M. Bengieser, R. Böttger, R. F. Marchand, J. Pelouze, and U. J. J. Leverrier—frequently observed that a reddish-coloured substance was formed along with ordinary phosphorus, and they usually attributed this to the formation of a lower oxide. E. Kopp observed, in 1844, during the preparation of ethyl iodide from phosphorus, iodine, and alcohol, that a red pulverulent residue was obtained which during the distillation passed into ordinary phosphorus. He referred to it as *Phosphor in der roten Modifikation.* J. J. Berzelius, in 1843, alleged that the red phosphorus insoluble in carbon disulphide which has been obtained by previous workers—*e.g.* by H. A. von Vogel by the action of sunlight on phosphorus—is an allotropic modification of phosphorus. Hence, R. Winderlich maintained that H. A. von Vogel, and J. J. Berzelius are the discoverers of allotropic phosphorus. The proof, however, was wanting. J. Nicklès

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discussed the history of the so-called amorphous phosphorus. In 1848, A. Schrötter demonstrated that in most cases the red substance is nothing but pure phosphorus in a peculiar state of aggregation—*ein neuer allotropischer Zustand des Phosphors.*

A. Schötter showed that ordinary phosphorus can be converted into the red form in a variety of ways. Thus, it is formed when phosphorus is exposed to *light* either under water or alcohol, in vacuo, in hydrogen, nitrogen, carbon dioxide, or in a hydrocarbon. The depth of penetration of the red film increases with the intensity of the light. F. Scriba exposed to sunlight a rod of phosphorus, half of which was wrapped round with tin-foil, and found the exposed part was alone transformed into red phosphorus. Observations on the reddening of phosphorus in light were made by H. A. von Vogel, C. W. Böckmann, A. Pedler, H. Reinsch, E. Riegel, and J. W. Retgers. The formation of red phosphorus by exposing to light a soln. of phosphorus in carbon disulphide, benzene, or chloroform was observed by A. Lallemand, A. Pedler, and A. Michaelis and K. von Arend. The last-named also observed that if the solvent be carbon tetrachloride, the red phosphorus produced contains some carbon ; and that if the insolated phosphorus be under water, some phosphorus tetritoxide is formed. W. A. Wahl found that a drop of yellow phosphorus under water immediately receives a coating of red phosphorus when illuminated by a quartz mercury lamp. When yellow phosphorus is placed in the ultramicroscope, either as a solid, or dissolved in carbon disulphide, the dark field becomes illuminated with submicroscopic points which increase in size and brightness, finally becoming red in colour. H. Siedentopf inferred from this that an intermediate, colloidal phase is formed during the passage from yellow to red phosphorus. W. R. Grove found that red phosphorus is produced when an *electric discharge* is sent through the vapour of ordinary phosphorus; and H. Geissler, V. Kohlschütter and A. Frumkin, and W. Hittorf made a similar observation—*vide infra*, colloidal phosphorus.

A. Schrötter showed that *heat* may convert ordinary phosphorus into the red form. He said that when heated in an atm. free from oxygen, sublimation begins at 150° without change of colour, but at about 226° ordinary phosphorus slowly passes into the red variety. After being heated to 240°–250°, for 50 hrs., the product is treated with carbon disulphide so as to wash out the ordinary phosphorus. The product is purified by boiling it with potash-lye of sp. gr. 1·3, and subsequently washing with water acidulated with nitric acid, and then with water alone. To remove the ordinary phosphorus, T. Weyl recommended boiling for 2 hrs. with 10 per cent. soda-lye. A. Stock and M. Rudolph also purified red phosphorus by treatment with alkali-lye. J. Nicklès recommended levigation of the mixture with carbon disulphide with a soln. of calcium chloride of sp. gr. 1·349–1·384—the soln. of ordinary phosphorus in the carbon disulphide floats, while the red phosphorus sinks in the calcium chloride soln. Several modifications of the process have been devised. V. Meyer heated a tube of the yellow phosphorus in the vapour of diphenylamine, at 310° ; L. Troost and P. Hautefeuille heated the sealed tube for 650 hrs. at 265° ; W. Muthmann, 24 hrs. at 230° ; J. W. Retgers, 24 hrs. at 240° ; and R. Schenck heated ordinary phosphorus in an atm. of hydrogen at 310°. A. Stock, H. Schräder, and E. Stamm found that the sudden quenching of phosphorus vapour at 900°–1175° furnishes red phosphorus. B. C. Brodie found that the reaction is accelerated by a trace of iodine. The reaction then progresses slowly at 100°, and with almost explosive violence at 200°. It is assumed that the iodine acts catalytically. There is a cyclic series of reactions in which the yellow phosphorus forms a subiodide which decomposes into red phosphorus and iodine. A. Besson held that phosphorus tetritatriiodide (*q.v.*) is the intermediate product ; R. Boulouch agreed with B. C. Brodie that the catalytic conversion of yellow to red phosphorus is due to the formation of the diiodide which in contact with an excess of phosphorus is converted into a subiodide which, at temp. above 160°, undergoes a series of decompositions resulting in the formation of the diiodide which immediately dissociates, forming red phosphorus. W. Hittorf did not accept this view of the conversion.

R. Schenck said that the initial change is a polymerization of P_4-mols. to P_8-mols.; and that the P_8-mols. are extremely labile, changing quickly into a more highly polymerized form. J. Böeseken does not believe that the catalytic action is due to the formation of a series of intermediate products, but considers that the transformation of yellow to red phosphorus is preceded by a decomposition of the P_4-mols. into P- or P_2-mols., which at once condense to the red form. The reactions are symbolized $P_4 \rightarrow 2P_2$; and $nP_2 \rightarrow P_{2n}$, in which the velocity of the second reaction is much greater than that of the first. The catalyst is supposed to hasten the dissociation of the P_4-mols. The reaction was discussed by W. Hittorf, R. Schenck, A. Besson, A. Pedler, and R. Boulouch; J. Böeseken found that aluminium chloride also stimulates the reaction. Red phosphorus is also produced when a soln. of phosphorus in carbon disulphide, benzene, toluene, or xylene, containing a little iodine, is boiled in a flash with a reflux-condenser. This reaction was discussed by B. Corenwinder, W. Hittorf, F. Rüdorff, and F. Todenhaupt. W. Hittorf said that selenium acts like iodine in accelerating the change; and F. Isambert found that red phosphorus mixed with some phosphorus sulphide, is formed when ordinary phosphorus is heated with a little sulphur or phosphorus sulphide.

N. Blondlot said that red phosphorus is formed by the action of soln. of potassium, sodium, or ammonium hydroxide on ordinary phosphorus; A. Commaille said that with aq. ammonia, some phosphorus hydride is formed—*vide infra*—and A. Stock and co-workers found that red phosphorus is produced by the aq. ammonia treatment. E. J. Houston considered the phosphorus produced by a protracted heating under potash-lye to be a special modification. B. Lepsius found that red phosphorus is formed when phosphine is decomposed by an electric arc; and A. Stock and co-workers, when the solid hydride is heated in vacuo for 24 hrs. at 340°–360°.

The manufacture of red phosphorus.—Red phosphorus is made commercially by heating yellow phosphorus in a glass or porcelain vessel embedded in sand placed in a large iron pan. The vessel containing the phosphorus is covered with an air-tight lid, and provided with a safety-valve dipping in water in case the press. inside the closed vessel becomes too great. When most of the air has been expelled, the safety-valve is closed, and the phosphorus is heated between 240° and 250° until it is converted into the red variety. If the temp. rises above 300°, there is a risk of explosion. When the conversion is effected in open iron vessels with a limited access of air, the process, though tedious, is said to be free from danger. The hard compact lumps of red phosphorus so obtained are ground with water, and boiled with sodium hydroxide soln. so as to remove the unaltered yellow phosphorus. The residual red phosphorus is then washed with boiling water, and dried, or preserved moist.

According to R. Schenck, when a soln. of yellow phosphorus in rectified phosphorus tribromide is maintained at 170°–190°, red phosphorus is slowly deposited. The transformation does not occur in very conc. soln., and a conc. of about 1 per cent. is favourable. A trace of phosphorus tetraiodide trebles the velocity of the reaction, without otherwise affecting the character of the change. R. Schenck thought the reaction is bimolecular, but when the disturbance due to the mechanical removal of the catalyst from the system by the precipitated red phosphorus was eliminated, the reaction was unimolecular. The precipitated phosphorus has a bright scarlet colour—**scarlet phosphorus**—and is an extremely finely divided form of red phosphorus. It resembles the form obtained by J. W. Retgers from liquid yellow phosphorus at temp. below 250°, and also with the red phosphorus precipitated by light from carbon disulphide soln. J. Böeseken found that the scarlet variety is also produced if a soln. of phosphorus in benzene (or better, phosphorus trichloride) containing a little aluminium chloride is kept at the b.p. of the solvent for a few hours (or minutes respectively). R. Schenck regards scarlet phosphorus as an amorphous or colloidal variety of red phosphorus, related to ordinary red phosphorus much as precipitated silica is related to quartz.

W. Hittorf prepared **metallic or violet phosphorus** by heating phosphorus in contact with lead for 10 hrs. at a temp. near 500°. The phosphorus dissolves in the lead at the high temp., and on cooling separates from the lead in the form of small, dark, reddish-violet, rhombohedral crystals. The crystals can be separated from the lead by treatment with dil. nitric acid, which dissolves only the lead. The crystals are further purified by boiling them with hydrochloric acid. A. Stock and F. Gomolka recommended the following procedure:

W. Hittorf's phosphorus is best prepared by heating 3 grms. of pure phosphorus with 200 grms. of lead in a sealed hard glass tube, packed in sand, to 800° for 48 hrs. The glass is broken and removed in a freezing mixture, and the lead cleaned by brushing and by washing with hydrofluoric acid. As nitric acid attacks the phosphorus, the lead is best removed by electrolysis in acetic acid containing lead. The cathode is placed at the bottom of the vessel, a clock-glass being fixed below the rod. The residue thus obtained contains some lead, mechanically dislodged from the anode, and is purified by boiling with hydrochloric acid in an atm. of carbon dioxide, followed by treatment with hydrofluoric acid. The purest product still contains 1·5 per cent. of lead.

Bismuth may be used in place of lead, but it dissolves only one-fifth as much phosphorus, and the crystals obtained are less pure. The metals appear to be held in solid soln. Only very minute quantities of Hittorf's phosphorus are obtained by sublimation. According to L. Troost and P. Hautefeuille, the same variety is formed when red phosphorus is heated under press. to 580°. The work of A. Pedler, J. W. Retgers, and D. L. Chapman shows that this variety differs from ordinary red phosphorus only in the size and development of the crystals. *Fine-grained red phosphorus is scarlet phosphorus, while coarse-grained red phosphorus is metallic or violet phosphorus.* A number of other allotropes have been reported, but many of them are the result of a misinterpretation of facts, or of an incomplete knowledge of facts.

The so-called *liquid phosphorus* reported by T. de Grotthus,[3] H. Rose, J. Kallhofert, and E. J. Houston were shown by D. Gernez, and F. P. Venable and A. W. Belden to be under-cooled or surfused phosphorus.

Sometimes ordinary or yellow phosphorus is called *white phosphorus.* The term "white phosphorus" was formerly applied to the white skin or crust which appears on the surface of phosphorus which is confined under water in diffuse daylight. It was mentioned by C. Cagniard de la Tour. H. Rose supposed it to be pure white phosphorus, but J. Pelouze, J. W. Retgers, and R. F. Marchand supposed it to be a hydrated form of phosphorus; G. J. Mulder, a compound of phosphorus hydride and oxide; B. Franke, $P_4(OH)H$; A. Dupasquier, a compound of calcium oxide and phosphorus derived from lime in the water; and E. Baudrimont, to an irregular corrosion of the surface of the phosphorus by the oxygen dissolved in the water. R. Böttger obtained it by cooling phosphorus which had been melted under an alcoholic soln. of potassium hydroxide; and R. Napoli obtained an opaque form by melting phosphorus under water at 50°.

In 1788, P. I. Bonz mentioned a black variety—*vide supra*—which came to be called *black phosphorus.* L. J. Thénard prepared what he called *phosphore noir* by suddenly cooling phosphorus at 70°. N. Blondlot supposed the coloration to be due to the presence of impurities, and he was able to imitate the effect by melting phosphorus in the presence of mercury or mercurial compounds; and this was confirmed by C. H. Hall, and D. Gernez. E. J. Maumené observed the production of black phosphorus among the first drops collected when phosphorus is distilled in a current of hydrogen prepared from zinc and sulphuric acid, but not in a current of carbon dioxide. F. A. Flückiger attributed E. J. Maumené's result to the presence of arsine in the hydrogen employed. E. Ritter supposed the coloration is produced by arsenic—*vide supra*, F. B. Fittica—but E. Reichardt said that arsenic is not necessary for the blackening of phosphorus. R. Wild said the blackening occurs with phosphorus which has been kept under water in a lead vessel; and W. N. Rae observed a case due to traces of copper salts in the water under which the yellow phosphorus was preserved. P. Thénard attributed the black colour to the presence of red phosphorus. The work of A. Schrötter, J. W. Retgers, R. Schenck, and A. Stock lends no support to the view that a distinct allotropic form of phosphorus is involved in these observations.

I. Remsen and E. H. Keiser considered that they had obtained a special allotropic form of phosphorus by suddenly cooling the vapour of phosphorus by iced-water. The product is here red phosphorus, for, as shown by A. Stock and co-workers, red phosphorus can be produced by suddenly quenching phosphorus vapour at 900°–1175°. H. M. Vernon reported that *rhombic phosphorus, i.e.* rhombic crystals of phosphorus, can be obtained by slowly cooling liquid phosphorus. This observation, however, remains unverified;

S. U. Pickering and A. E. H. Tutton could not produce the rhombic form. P. Jolibois obtained what he called a polymorphous form of red phosphorus stable below 450°, but there is nothing to show that this is essentially different from ordinary red phosphorus.

E. Cohen and K. Inouye[3] observed no sign of the formation of an allotropic form of yellow phosphorus at low temp.; but P. W. Bridgman observed the formation of an allotropic modification of ordinary yellow phosphorus during some experiments on the effect of high press. on ordinary phosphorus. This variety is formed when yellow phosphorus at 60° is compressed under 11,000 kgrms. per sq. cm., and there is a transition point at —76·9° which is readily shown by the terrace in the heating curve of phosphorus as it rises in temp. from —90°, Fig. 2. There is also a vol. contraction of about 2 per cent. during the change. The crystalline form of the **β-yellow phosphorus** is probably hexagonal, whereas ordinary, or **α-yellow phosphorus** is cubic. D. Vorländer and co-workers gave —68° for the transition temp., and they were unable to obtain well-defined crystals, but thought that they are either monoclinic or rhombic.

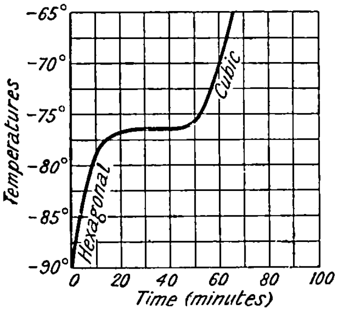

FIG. 2.—Heating Curve during Passage from α- to β-yellow Phosphorus.

Again, in attempting to change yellow into red phosphorus by the application of press., P. W. Bridgman found that a denser crystalline variety is formed at 200°, with press. ranging from 12,000 to 13,000 kgrms. per sq. cm. This variety is called **black phosphorus**; and it is not to be confused with older black or dirty phosphorus. The change is irreversible, since black phosphorus is more stable than red. Ordinary yellow phosphorus has a sp. gr. of 1·83 to 1·85; red phosphorus, 2·05 to 2·39; and black phosphorus approximates 2·69, that is, 15 per cent. higher than the densest red phosphorus. He did not succeed in converting yellow into black phosphorus at 175°, and a press. of 13,000 kgrms. per sq. cm., although at higher press. the change would probably occur, because at 200° the conversion was successful. At 200°, yellow phosphorus is converted into the red modification, using a little sodium as catalyst and a press. of 4000 kgrms. per sq. cm. The chemical properties of black phosphorus are very much like those of red phosphorus—both varieties are insoluble in carbon disulphide; they are attacked by cold nitric acid, and they resist the action of cold sulphuric acid. Black phosphorus ignites at nearly 400° in air, and, unlike red phosphorus, it is not ignited when struck on an anvil with a hammer. When heated in a closed glass tube, it vaporizes, and the vapours condense to a mixture of white and red phosphorus, hence it is probable that the vapours from both black and red phosphorus are nearly alike. The black variety, unlike yellow or red phosphorus, is a fairly good conductor of electricity, and the conductivity increases rapidly with rise of temp. It is also a better conductor of heat, and is less diamagnetic than either red or yellow phosphorus. Black phosphorus under press. can be melted at a rather higher temp. than red phosphorus similarly treated, and on cooling, both varieties solidify to a chocolate-brown mass of sp. gr. 2·18. C. H. Hall, and A. Smits and co-workers support the view that P. W. Bridgman's black phosphorus is a true allotrope. The former held that L. J. Thénard's black phosphorus was a colloidal suspension of mercury in phosphorus. W. Ipatieff and W. Nikolaieff observed that a purple, crystalline phosphorus is produced when yellow phosphorus is heated with water at 248° and at a press. of 48 atm. It is soluble in carbon disulphide; over 216° and 89 atm. press., black crystalline phosphorus, insoluble in carbon disulphide, is formed. When red phosphorus is heated in hydrogen at 200° and 90 atm. press., W. Ipatieff found that black phosphorus is formed. W. Marckwald and K. Helmholtz found black phosphorus changes into the scarlet form at 575°.

A. Müller[4] prepared **colloidal red phosphorus** by boiling the commercial product for some time, with water, and after allowing the mixture to stand some time, pouring off that remaining in suspension. This was repeated a number of times. Colloidal soln. with high viscosity—produced by additions of the colloid gelatin, gum, starch, casein, albumin, glue, dextrin, or sugar—are flocculated with difficulty on adding sodium chloride. Thus, with 50 c.c. of the phosphorus suspension, and 5 c.c. of a 10 per cent. soln. of sodium chloride :

	After 24 hrs.	After 48 hrs.
No colloid	clear	clear
Gelatin : 10 c.c. of 5 per cent. soln. . .	very turbid	very turbid
Gelatin : 5 c.c. of 5 per cent. soln. . .	turbid	turbid
Dextrin : 10 c.c. of 5 per cent. soln. . .	turbid	nearly clear
Sucrose : 10 c.c. of 5 per cent. soln. . .	slightly turbid	clear
Sucrose : 10 c.c. of 25 per cent. soln. .	very turbid	turbid

The viscosity of the medium protects the suspension against gravitational and electrical forces. T. Svedberg prepared colloidal soln. of red phosphorus in isobutyl alcohol by sending a series of small arc discharges about the red phosphorus immersed in the medium. P. P. von Weimarn obtained **colloidal yellow phosphorus** by pouring an alcoholic soln. into a great excess of water. A. Lottermoser found the ethereal soln. was clear and colourless, but in diffuse daylight it had an orange-yellow opalescence, and in transmitted light it appeared clear and yellowish-red—*vide supra*, scarlet phosphorus. V. Kohlschütter and A. Frumkin found that when an electric discharge is passed through yellow phosphorus vapour, red phosphorus is deposited in a highly dispersed condition on the walls of the containing vessel. The deposit is loosened in the presence of indifferent gases—hydrogen, argon, helium, and nitrogen—and more so in the case of argon than of helium. Hydrogen and nitrogen react chemically with the gas ; argon and helium are absorbed. When the deposit is heated, it forms ordinary red phosphorus. The deposit formed at first is considered to be identical with the product obtained by suddenly cooling the superheated phosphorus vapour, and when heated, this sinters and passes with ordinary red phosphorus, and has the appearance of a homogeneous, dried gel of stannic oxide.

A review of the alleged allotropes of phosphorus reduces their number to four, namely, the α- and β-forms of yellow phosphorus, red or violet phosphorus, and black phosphorus. Most of the work of various investigators has been directed towards elucidating the nature of red phosphorus, and of the transformation of yellow to red phosphorus and conversely. Red phosphorus was formerly considered to be amorphous, and it was often called amorphous phosphorus. The term "amorphous," however, here referred more to the general appearance of the powder rather than to its minute structure. J. W. Retgers[5] showed that the particles of ordinary red phosphorus are rhombohedral crystals, which are well developed in those of W. Hittorf's violet phosphorus. All four varieties are therefore crystalline. J. W. Terwen has reviewed this subject in a general way ; and M. Copisarow discussed the theory of allotropy.

P. Jolibois found that the velocity of transformation of yellow to red phosphorus increases with the temp. It is very slow at 360°, but it can be observed at 250° if a trace of iodine as catalyst be present. G. Lemoine investigated the transformation of yellow to red and red to yellow under the influence of heat, and he concluded that the transformations are reciprocal ; and that a balanced reaction is involved. If yellow phosphorus be heated in a sealed glass tube to 440°, a state of equilibrium is attained between the yellow and red phosphorus : $P_{yellow} \rightleftharpoons P_{red}$. The slopes of the curves in Fig. 3 illustrate the speeds

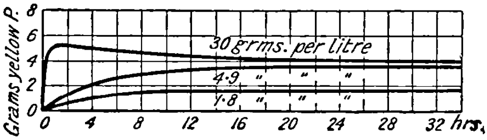

FIG. 3.—Speed of Transformation of Red to Yellow Phosphorus (Diagrammatic).

of transformation of red to yellow phosphorus in closed vessels containing initially 1·8, 4·9, and 30 grms. per litre of space. The experiments were made by heating the vessels to the specified temp. and time, and then suddenly quenching the vessel. Similar results were obtained in the conversion of yellow to red phosphorus. The actual values depended upon the amount of phosphorus in unit vol., and on the capacity of the containing vessel. This shows that the surface of the containing vessel plays some part in the reaction. The results follow the mass-law, $dx/dt=k(a-x)$, where k, the velocity constant=0·31 for one set of experiments with red to yellow phosphorus, for the converse change the velocity constant is 0·041 nearly. There is an anomaly when a large proportion of phosphorus is present in the vessels, for the yellow phosphorus condensed from the vapour attains a maximum and then decreases instead of remaining constant with time. L. Troost and P. Hautefeuille showed that the properties of red phosphorus depend on the temp. at which it is produced; and the variety peculiar to the particular temp. at which it is produced is acquired only slowly. The vap. press., for example, is higher the lower the temp. at which the red phosphorus has been prepared. Thus red phosphorus prepared at 265° behaves with respect to that prepared at 440°, as white phosphorus acts with respect to red. This, said P. Duhem, means that varieties of red phosphorus prepared at a low temp. should be regarded as existing in a state of *faux equilibre*, and when they are brought to a higher temp., they change into the variety corresponding with this temp.

A. Colson showed that there is no common solvent for red and yellow phosphorus. He studied the rate of conversion of yellow into red phosphorus when the former is dissolved in turpentine or in carbon disulphide. The rate of conversion follows the same laws as when phosphorus alone is heated, and is dependent on the temp. and conc. of the soln. For example, a soln. of phosphorus in oil of turpentine, containing 23 grms. per litre, remained clear after heating for 52 hrs. at 230°–235°, but gave a thick deposit of red phosphorus after heating for 8 to 10 hrs. at 285°–290°. A soln. containing 20 grms. of phosphorus in a litre of oil of turpentine, deposited red phosphorus after heating for 55 hrs. at 260°–265°, whilst a soln. of phosphorus in carbon disulphide, containing 90 grms. per litre, deposited red phosphorus after heating for 15 hrs. at the same temp. Three tubes containing respectively 150, 125, and 10 grms. of phosphorus in 100 grms. of carbon disulphide were heated at 225°–230°; at the end of 4 hrs. the first tube contained a large quantity of red phosphorus, the second tube contained traces of the red phosphorus, whilst the contents of the third tube were unaltered. He said that the slow irreversible change of yellow to red phosphorus in turpentine soln. at 250°, is due to the formation of small quantities of hydrogen phosphide and its subsequent decomposition into red phosphorus to form a further quantity of hydrogen phosphide. A 2 per cent. soln. of phosphorus in oil of turpentine was sealed in a tube with hydrogen phosphide and enclosed in a tube containing a further quantity of the soln. After heating at 240° for 4 hrs., the inner tube contained a copious deposit of red phosphorus, whilst the contents of the outer tube remained clear even after 12 hrs. at 250°. Phosphorus dissolved in an oxygenated solvent, such as ethyl benzoate, does not undergo any allotropic transformation even when the soln. is heated at 305°–310° for 25 hrs.

The density of the vapour from red or yellow phosphorus is the same, and it corresponds with the mol. P_4; hence, from the analogy between a vapour and a solute —1. 10, 8—it might be inferred that the two varieties of phosphorus would become identical in a common solvent. If a soln. of yellow phosphorus in phosphorus tribromide—with a trace of iodine as catalytic agent—is kept between 170° and 190°, red phosphorus is gradually deposited. R. Schenck measured the conc. of the yellow phosphorus in soln. after the lapse of different intervals of time, and found the reaction to be bimolecular, but when allowance is made for the mechanical removal of the catalytic agent from the soln. by the precipitated red phosphorus, the reaction is unimolecular.

Violet phosphorus is the stable form at ordinary temp. and yellow phosphorus the unstable modification. The reason the yellow phosphorus does not pass into the violet form at ordinary temp. is due to the extremely slow velocity of the change. By the distillation of violet phosphorus at 290°, yellow phosphorus is obtained, and at ordinary press. the transition-point of the stable violet into the unstable yellow is masked by the vaporization of the phosphorus. According to A. Stock and F. Gomolka, when violet phosphorus is heated under press. in capillary tubes so as to prevent distillation, it forms a yellow fluid at 610°, and red particles begin to separate from the cooling soln. at 580°. At 570°, the mass turns red. Violet phosphorus begins to melt at 589·9°. The vap. press. of yellow phosphorus is greater than the red; under ordinary conditions the curves cannot be carried above 400° because the yellow phosphorus passes into the violet variety so very quickly. A. Smits and S. C. Bokhorst's two vap. press. curves are illustrated in Figs. 4 and 5. Both vap. press. curves converge towards the transition point as is the case with allotropic modifications of other elements. It is inferred that both varieties would be in equilibrium with the vapour phase at the transition point—589·9°—were it possible to make the experiment. The vaporization of phosphorus is therefore a complex phenomenon. If violet phosphorus be heated in a closed space to a given temp. until its vap. press. is constant, and then heated to a higher temp. until a greater vap. press. is reached, on cooling, the vap. press. does not return to its original value, but lags behind, thus making it probable that the vaporization is not to be explained by a simple dynamic equilibrium between the streams of mols. approaching and departing from the surface of separation between the two phases. In explanation, it is supposed that the vaporization of phosphorus involves the reversible process of true vaporization together with a rapid irreversible polymerization of the mols. of the vapour.

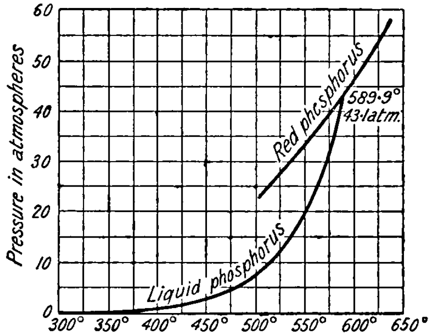

Fig. 4.—Vapour Pressure Curve of Liquid Phosphorus and Sublimation Curve of Red Phosphorus.

The term "red phosphorus" includes a large number of products with properties which differ more or less from one another, and depend upon the temp. at which the substance was formed. W. Hittorf's violet phosphorus, crystallized from molten lead, stands at one end of the series, and scarlet phosphorus stands at the other end. E. Cohen and J. Olie consider ordinary red phosphorus to be an isomorphous mixture or solid soln. of yellow and violet phosphorus in dynamic equilibrium: $P_{yellow}=P_{violet}$, where the equilibrium constant depends upon the temp. One objection has been made to this hypothesis: the denser varieties prepared at high temperatures do not assume an appropriate lower density when kept for a long time at lower temp. The answer may be that the equilibrium condition is very slowly attained at the lower temp. or that the reverse change is arrested by what P. W. Bridgman calls *frictional passive resistance.* Increase of temperature lessens the frictional resistance and the change can proceed further. This hypothesis explains: (i) Why the reverse change does not occur on cooling; (ii) Why the nuclei formed during the change from yellow to red phosphorus do not increase in size, but rather increase in number; (iii) Why the sp. gr. of red phosphorus prepared at different temp. vary—thus the sp. gr. of R. Schenck's variety formed at 30° is 2·05, and W. Hittorf's variety has a sp. gr. of 2·39; (iv) Why red phosphorus does not melt sharply like a pure chemical individual, but rather melts over an interval of temp. like a solid soln.—thus, according to A. Stock and O. Johannsen, red phosphorus melts between 600° and 615°, and violet phosphorus between 620°

and 625° ; (v) Why the vap. press. of yellow phosphorus remains constant, when it is heated, until all the yellow phosphorus has disappeared ; instead of changing abruptly to that of the red, the change diminishes quite rapidly ; and (vi) Why the amount of heat developed by the combustion of red phosphorus is not constant, but varies with the different varieties. Hence, it is inferred that **red phosphorus is not a single homogeneous species, but rather a transitional product formed during the passage of yellow to violet phosphorus.** In agreement with L. Troost and P. Hautefeuille, A. Stock made the counter-suggestion that red phosphorus is a solid soln. of several varieties of red phosphorus in each other. J. Böeseken said that red phosphorus is a mixture of much violet phosphorus with a little colloidal phosphorus. A. Smits and S. C. Bokhorst also developed the hypothesis that red phosphorus is a mixture of two or more kinds of mols. in equilibrium. As pointed out by A. Stock and F. Gomolka, the heterogeneous character of red phosphorus really means that many of the measurements of the physical constants of this substance have *nicht geringste Wert.* W. Puttfarcken found some lower oxide in commercial red phosphorus.

H. W. B. Roozeboom suggested that the relations between white and red phosphorus may be like those of cyanogen, and that the vap. press. curve of liquid yellow phosphorus may terminate below the m.p. of the violet form ; he also said that it may be that liquid yellow phosphorus is super-cooled violet phosphorus. A. Smits and co-workers showed that liquid yellow phosphorus is to be taken as super-cooled liquid violet phosphorus. It is usual to consider under-cooled liquids as being still in the liquid state, and since yellow phosphorus crystallizes in the cubic system, it is necessary to modify the ordinary meanings of some of these terms. A. Smits and co-workers represent the press.-temp. diagram of the phosphorus system schematically by Fig. 5. Here the curve *RC′* represents the vap. press. of violet phosphorus at different temp. ; *C′E*, the vap. press. curve of liquid phosphorus ; *C′C″*, the effect of press. on the m.p. of violet phosphorus; *C″C‴*, the effect of press. on the m.p. of black phosphorus ; *C″D*, the effect of press. on the transition point of violet to black phosphorus. If molten phosphorus be cooled below the temp. at which it is converted into violet phosphorus, the curve *B′C′E* represents the vap. press. curve of liquid yellow phosphorus ; *B′*, the m.p. of α-yellow phosphorus ; *B′B″*, the effect of press. on the m.p. of α-yellow phosphorus ; *A′B′*, the vap. press of ordinary yellow phosphorus ; *WA′*, the vap. press. of β-yellow phosphorus ; *A′A″*, the effect of press. on the transition temp. of α- into β-yellow phosphorus. When molten phosphorus cooling from the state represented by *E* reaches the state represented by *C′*, it may remain liquid, passing through the states *C′B′*, or it may pass into violet phosphorus assuming the states represented by *C′R.*

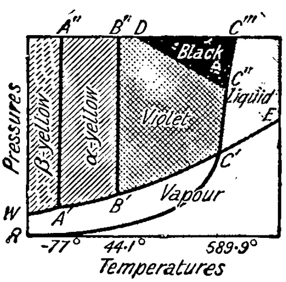

FIG. 5.—Diagrammatic Representation of the Different Allotropic States of Phosphorus.

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§ 5. The Physical Properties of Phosphorus

As ordinarily prepared, phosphorus is a yellow solid with a waxy lustre. When well purified the so-called yellow or white phosphorus is colourless, and transparent if slowly cooled, and more or less opaque if rapidly cooled. J. B. Trautwein,[1] and J. A. Buchner said that when cooled after fusion, yellow phosphorus may furnish large dodecahedral or octahedral **crystals**. According to J. W. Retgers, if a rod of yellow phosphorus is broken, the crystalline structure of the fractured surfaces recalls that of a broken zinc rod. N. Blondlot, W. D. Herman, G. Whewell, and C. A. Burghardt described the preparation of crystals of phosphorus from molten phosphorus. E. Mitscherlich obtained crystals by sublimation in a sealed tube containing an inert gas, and kept warm for a few days. B. Pelletier said that soln. of phosphorus in volatile oils yield octahedral crystals; and E. Mitscherlich, that soln. in phosphorus sulphide furnish dodecahedral crystals. J. W. Retgers found that soln. of phosphorus in turpentine, oil of aniseed, oil of lemons, or oil of almonds give combinations of the dodecahedron and cube; while the crystals obtained by cooling warm conc. soln. in carbon disulphide, benzene, xylene, alcohol, ether, methylene iodide, and petroleum give dodecahedral crystals which are almost always columnar. Very good crystals were obtained from methylene iodide, and carbon disulphide; T. Bokorny obtained good crystals by adding alcohol or ether to a carbon disulphide soln. of phosphorus, and pouring the soln. into cold water; and A. C. Christomanos obtained octahedral or doubled tetrahedral crystals by evaporating ethereal soln., and thick prisms, or needles from a benzene soln. O. Lehmann described skeletal crystals. The different forms of the cubic crystals were measured by N. S. Maskelyne, and E. Mitscherlich; P. W. Bridgman's β-yellow phosphorus is hexagonal, while the ordinary or α-yellow phosphorus is cubic.

According to L. Troost and P. Hautefeuille, the colour of red phosphorus varies with the temp. of preparation for that prepared at low temp. is scarlet, and that at a high temp. has a violet or purple tinge; while that at a still higher temp. is almost black. Red phosphorus was considered by A. Schrötter to be amorphous, but W. Muthmann, and J. W. Retgers showed that while a little amorphous phosphorus may be present the bulk of the material consists of doubly refracting crystals. The crystalline nature of red phosphorus was confirmed by A. Pedler, L. Troost and P. Hautefeuille, J. Böeseken, D. L. Chapman, A. Stock, and H. Arctowsky. As indicated above, red phosphorus ranges from the possible colloidal, scarlet phosphorus of R. Schenck to the so-called metallic or violet phosphorus of W. Hittorf. R. Engel, and W. Hittorf suggested that the crystals are possibly isomorphous with those of arsenic, antimony, and bismuth; but, according to

G. Linck, the crystals are trigonal with the axial ratio $a:c=1:1·1308$, and are not eutropic nor isomorphous with those of arsenic, antimony, and bismuth; but G. Linck and P. Möller, A. Stock and co-workers, F. von Wolff, and O. Johannsen regarded the crystals as monoclinic. This makes yellow phosphorus analogous with the cubic forms of antimony and arsenic; and red phosphorus with monoclinic antimony and arsenic. H. C. Burger, and S. von Olshausen obtained an **X-radiogram** of red phosphorus, but no detailed study has been made of the result; although S. von Olshausen inferred that it has a simple cubic lattice of side $a=7·331$ A. P. W. Bridgman's black phosphorus is crystalline. G. Linck and H. Jung found the X-radiogram of black phosphorus, like that of arsenic, antimony, and bismuth, corresponds with the trigonal or rhombohedral space lattice with $a=5·96$ A., and $\alpha=60°\ 47'$. There are 8 atoms per unit cell. D. Gernez found the **velocity of crystallization** of the under-cooled liquid is 1·2 units at 43·8°, 56·9 units at 41·4°, 243·1 units at 38°, and 1030·9 units at 24·9°.

C. W. Böckmann[2] gave 1·896 for the **specific gravity** of yellow phosphorus; A. F. de Fourcroy and L. N. Vauquelin, 2·0332; A. Wigand, 1·828; while A. Schrötter gave 1·826–1·840. For the value at 0°, G. Quincke gave 1·986; G. Pisati and G. de Franchis, 1·83676, and G. Vincentini and D. Omodei, 1·83676, and at 4·44°, 1·80654; at 10°, H. Kopp gave 1·826; at 13°, B. C. Damien, 1·8177, and H. M. Vernon, 1·814; at 17°, R. Böttger, 2·0332; at 18°, J. Böeseken, 1·831; at 20°, G. Pisati and G. de Franchis, 1·82321; at 24·2°/4°, B. C. Damien gave 1·828; at 35°, J. H. Gladstone and T. P. Dale gave 1·823; at 44°, G. Pisati and G. de Franchis gave 1·8068; and at 44·2°/4°, B. C. Damien gave 1·814. J. Böeseken gave for phosphorus purified by distillation in vacuo, 1·831 at 18°. For liquid phosphorus, J. H. Gladstone and T. P. Dale gave 1·763 at 35°; H. Kopp, 1·743 at 44°; G. Quincke, 1·833 at 43°; G. Vincentini and D. Omodei, 1·74529 at 44·4°; B. C. Damien, 1·7555 at 44·2/4°; G. Pisati and G. de Franchis, 1·74924 at 40°; 1·69490 at 100°; 1·60270 at 200°; and 1·52867 at 280°; and W. Ramsay and O. Masson, 1·4850 at the b.p. Observations were also made by A. Schrötter, and F. C. O. von Feilitzsch. G. A. Erman found the sp. gr. of yellow phosphorus just before melting to be 1·8121, and just after, 1·7560. According to P. W. Bridgman, the sp. gr. of β-yellow phosphorus corresponds with a contraction of 2 per cent. during its formation from ordinary or α-yellow phosphorus with a sp. gr. of 1·83–1·85.

For the sp. gr. of red phosphorus, A. Schrötter gave 1·964 at 10°, and 2·089–2·106 at 17°; J. Böeseken, 2·31–2·34; A. Wigand, 2·296; B. C. Brodie, 2·14–2·23; G. Linck and P. Möller, 2·18–2·29 at 16°–19°; A. Colson, 2·094; A. Stock and co-workers, 2·14 at 17°, and 2·17 at 22°, when for scarlet phosphorus under similar conditions the sp. gr. was 2·02–2·05, and for violet or metallic phosphorus, 2·35–2·37 at 22°. E. Cohen and J. Olie gave 2·18–2·23 for red phosphorus at 18°/4°, and 2·23–2·24 at 18°/4° for violet phosphorus. P. Jolibois found the sp. gr. of slowly cooled red phosphorus to be 2·27. L. Troost and P. Hautefeuille showed that the sp. gr. of red phosphorus is dependent on the temp. at which it has been prepared. Thus, for that prepared at 265° he obtained 2·148 at 0°; at 360°, 2·19 at 0°; at 500°, 2·293 at 0°; and at 580°, 2·34 at 0°. W. Hittorf, and G. Linck gave 2·34 at 15·5° for the sp. gr. of violet or metallic phosphorus; A. Smits and co-workers, 2·21–2·34; and A. Stock and F. Gomolka, 2·39 for crystals with 3·5 per cent. of lead; 2·36 for crystals with 1·5 per cent. of lead; and 2·36–2·37 for crystals prepared with bismuth in place of lead. P. W. Bridgman gave 2·699 for the sp. gr. of black phosphorus. This constant is thus 15 per cent. higher than that of any of the other allotropic forms of phosphorus. The best representative values of the sp. gr. of the four allotropic forms of phosphorus are:

	β-yellow.	α-yellow.	Violet.	Black.
Sp. gr. . .	1·88	1·84	2·34	2·699

H. Buff gave 25 for the calculated **atomic volume** of tervalent phosphorus, and

22 for quinquevalent phosphorus; and T. E. Thorpe gave 25·3. E. Petersen gave 17·0 for the at. vol. of yellow phosphorus, and 14·7 for red phosphorus. T. E. Thorpe, H. Buff, and J. I. Pierre calculated the at. vol. of phosphorus in combination as PCl_3, PBr_3, $POCl_3$, $PSCl_3$, $POBrCl_2$, and $PCl_2.C_2H_5OH$ to range from 24·0 to 26·1; that of free phosphorus, by G. Pisati and G. de Franchis, is 20·2. I. I. Saslowsky gave 2·34 for the sp. gr. at room temp., and 13·3 for the at. vol. W. Ramsay and O. Masson gave 20·91 for the at. vol. of the free element, and 25·3 for the combined element. H. Buff suggested that the sp. vol. of phosphorus in combination varies with the valency. Accepting H. Kopp's value of 7·8 for singly linked oxygen atoms, and 12·2 for the doubly linked atoms, T. E. Thorpe and A. E. H. Tutton calculated that at. vol. of phosphorus in phosphorous oxide to be 20·9—about the same value as that of free phosphorus. S. Sugden studied this subject. E. B. R. Prideaux gave 20·04 for the at. vol. of the liquid at 290°, and he calculated 15·1 for the at. vol. of quinquevalent phosphorus, and 25·06 for the tervalent element. He calculated the at. vol. of phosphorus in some different combinations to be:

	PCl_3	PBr_3	PCl_5	PBr_5	$POCl_3$	$POCl_2Br$
At. vol. . .	25·1	28·4	15·1	23·3	18·9	21·0

W. A. Kowalewsky gave 18·09–23·31 for the at. vol. of phosphorus in the alkyl phosphates. T. W. Richards found the at. vol. under 493·5 atm. press. is 14·4. For the observed **specific volume** of the solid, A. Hess gave 0·55399, and 0·57305 for the liquid—this corresponds with an expansion of 3·44 per cent. W. Ramsay and O. Masson found the sp. vol. at the b.p. to be 0·6734. E. Donath and J. Mayrhofer made some observations on this subject. G. Tammann gave for the change of volume, δv c.c., on melting at 50·03°, 69·98°, 90·21°, and 100·18°, and respectively 220, 959, 1720, and 2155 atm. press., the respective values of δv $=0·01862$, 0·01756, 0·01579, and 0·01478 c.c.; or $\delta v=0·01908-0·000077(\theta-43·9)$. A. Hess gave 0·0190 c.c. per gram; H. Kopp, 0·01894 c.c.; B. C. Damien, 0·0179; G. Pisati and G. de Franchis, 0·01939; and A. Leduc, 0·0191. P. W. Bridgman's values of δv are indicated below. G. le Bas showed the approximate convergence of the temp.-vol. curves of the liquid and solid states towards absolute zero. A. Smits and S. C. Bokhorst calculated the value of the constant b of **J. D. van der Waals' equation.** This when taken to represent the size of the molecule becomes 0·00539, at the critical temp.; the corresponding value calculated for the phosphorus atom in phosphine is 0·00124; so that there are $0·00539/0·00124=4·33$ atoms in the molecule. This is taken to indicate a slight association of the P_4-mols. J. J. van Laar calculated for b of J. D. van der Waals' equation, $b=0·00140$; for a, $\sqrt{a}=0·066$; and for the valency attraction A, $\sqrt{A}=33$. M. Trautz calculated 20×10^{-8} cm. for the **molecular diameter** of phosphorus. B. Cabrera calculated 1·11 A. to 1·37 A. for the at. radius of P'''. W. P. Davey, and C. del Fresno studied the at. vol. of phosphorus; and S. Mokruschin, the mol. diameter at the b.p.

A. W. Williamson[3] gave 2·805 grms. for the weight of a litre of phosphorus vapour calculated for normal conditions. J. B. A. Dumas obtained 4·42 for the **vapour density** of phosphorus vapour when the value calculated for P_4 is 4·3; E. Mitscherlich gave 4·58; and H. St. C. Deville and L. Troost found 4·35 at 500°, and 4·50 at 1040°; while J. Mensching and V. Meyer gave 4·16 for the vapour density at a red-heat; and 3·03 at a white-heat, while H. Biltz and V. Meyer obtained 3·632 at 1484°; 3·226 at 1677°; and 3·147 at 1708°. The vap. density, said V. Meyer, is considerably less than corresponds with the P_4-mol at elevated temp., and at a white-heat approximates to the value required for P_2. G. Preuner and J. Brockmöller made observations on this subject; they found the total press., P, at temp. between 500° and 1200°, at constant vol., with the amounts of red phosphorus calculated in grams per c.c., shown in Fig. 6. The corresponding partial press. for p_4 of P_4; p_2 of P_2; and p of P are indicated in Table II.

TABLE II.—PARTIAL PRESSURES DUE TO P_4-, P_2-, AND P-MOLECULES.

Total press. P mm.	800°			1000°			1200°		
	p_4	p_2	p	p_4	p_2	p	p_4	p_2	p
5	1·7	1·6	1·6	0·01	1·2	3·8	0·01	1·0	4·0
10	3·8	4·0	2·2	0·01	4·0	6·0	0·2	2·0	7·0
20	11·0	6·0	3·0	2·0	9·0	9·0	0·2	6·0	14·0
30	19·0	8·0	3·1	5·0	11·0	14·0	1·0	10·5	18·5
40	24·9	10·2	3·3	8·0	13·0	19·0	2·0	14·0	24·0
50	33·6	13·0	3·4	12·0	15·0	23·0	3·0	20·0	27·0
60	41·4	15·0	3·6	17·0	37·0	16·0	4·5	26·0	39·0
70	49·0	17·0	4·0	22·0	31·0	17·0	6·0	32·0	32·0
80	57·5	18·0	4·5	28·0	34·0	18·0	7·5	36·0	36·5
90	66·0	19·0	5·0	35·0	37·0	18·0	9·5	42·0	39·0
100	74·9	20·0	5·1	40·5	40·5	19·0	11·0	48·0	42·0
150	122·0	22·0	6·0	71·0	54·0	25·0	25·0	74·0	51·0
200	169·0	25·0	6·0	109·0	62·0	26·0	45·0	94·0	59·0
300	260·0	33·0	6·5	268·0	102·0	30·0	86·0	143·0	71·0
600	549·0	44·0	7·5	440·0	128·0	32·0	259·0	245·0	96·0
750	692·0	50·0	8·0	576·0	142·0	35·0	361·0	283·0	106·0

The average number of atoms, i, per molecule is as follows :

800°	P . .	37	84	158	349	470	482 mm.
	i . .	2·90	3·51	3·72	3·75	3·84	3·87
1000°	P . .	58	123	225	290	458	64·4 mm.
	i . .	2·20	2·77	3·07	3·18	3·27	3·42
1200°	P . .	88	187	346	440	617	890 mm.
	i . .	1·65	2·05	2·29	2·35	2·73	2·83

The calculated thermal values of the dissociation $P_4=2P_2$ are 30,200 cals. at 800° ; 30,000 cals. at 900° ; 28,500 cals. at 1000° ; and 28,000 cals. at 1100° ; and for the $P_2=2P$ transformation, 23,200 cals. between 800° and 1200°. The effect of temp. on the equilibrium constant K_4 for $P_4=2P_2$ is $\log (K_4/760)=-(29000+2T)/4{\cdot}75T+1{\cdot}75 \log T-1{\cdot}4$; and K_2 for $P_2=2P$ is $\log (K_2/760=-(23000+2T)/4{\cdot}75T+1{\cdot}75 \log T-3{\cdot}0$, where the chemical constant for the P_4-mol is —1·4, and for the P_2-mol, —3·0. The dissociation constants are :

	800°	900°	1000°	1100°	1200°
K_4	350	13·7	40·0	98·0	211
K_2	7·4	3·8	9·0	18·9	36·0

According to A. Stock and co-workers, the vap. density between 500° and 700° corresponds exactly with P_4-mols ; at higher temp. dissociation occurs, but at 1200° and 175 mm. press., only 61 per cent. is dissociated. Calculations agree with $P_4=2P_2$. Under atm. press., the dissociation is 0·01 at 800°, 0·1 at 1000°, and 0·33 at 1200° ; and under a press. of 0·25 atm., there is almost 66 per cent. dissociation at 1200°. S. Dushman studied the reactions : $P_2 \rightleftharpoons 2P$; and $P_4 \rightleftharpoons 2P_2$. R. Wegscheider and F. Kaufler argued that yellow and red phosphorus are not merely polymorphous, but that they are chemically different, because, if polymorphous, the liquid forms should be identical, and if violet phosphorus is the stable form, molten yellow phosphorus, or a sat. soln. of yellow phosphorus in carbon disulphide,

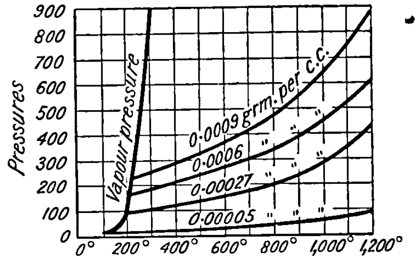
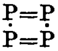


FIG. 6.—Dissociation Pressures of Phosphorus Vapour at Different Temperatures.

when sown with red phosphorus, should furnish red phosphorus, whereas no perceptible change occurs. According to D. L. Chapman, the vapours of ordinary and of red phosphorus are identical; and W. Ostwald suggested that phosphorus vapour is neither that of ordinary nor of violet phosphorus. K. Schaum said that this hypothesis applies only to phosphorus vapour at a high temp. At lower temp., in consequence of different rates of transformation, the vapours appear to be different. Again, when energy—actinic, thermal, or electrical—is added to the system, the vapour from ordinary phosphorus furnishes red phosphorus in agreement with the assumption that polymerization occurs during the formation of violet phosphorus. This, however, neither proves nor disproves the assumption that the vapours of violet and yellow phosphorus are different. W. R. Fielding discussed the polymerization of phosphorus.

G. Lemoine's work, previously cited, is in agreement with the assumption that in the vaporous state a balanced reaction is involved: $P_{yellow}=P_{violet}$. Contrary to the statement of H. Arctowsky, A. Stock and E. Stamm maintained that red phosphorus is not appreciably volatile at 100°, or even at 200°; and that the vapour of red phosphorus condenses partly as red phosphorus when heated at 280°–400°; and that the so-called metallic phosphorus of W. Hittorf, at 300°–350°, gives a vapour which condenses as yellow phosphorus even if it has been subjected to an intermediate heating at 500°. Colourless phosphorus also gives a colourless distillate. Hence, the vapour of red phosphorus must contain mols. peculiar to red phosphorus; in agreement with the observation of A. Stock and co-workers, that red phosphorus can be sublimed in the crystalline form. They also found in agreement with W. Hittorf that when phosphorus vapour is rapidly cooled, a portion is condensed as red phosphorus, and the proportion of red phosphorus deposited is greater the higher the temp. of the vapour before the chilling occurs. The duration of the heating has no appreciable effect, but the cooling of the vapour must be effected rapidly. The surface of the containing vessel has a catalytic influence on the quantity of red phosphorus formed by chilling the vapour, but comparative experiments by A. Stock and E. Stamm showed that the quantity of red phosphorus formed diminishes as the press. decreases; A. Stock and co-workers added that these facts are in agreement with the assumptions that (i) the two forms of phosphorus are chemically different; (ii) that red phosphorus is formed by the union of the dissociated mols of phosphorus either among themselves, or with the undissociated mols; and (iii) that the formation of the P_4-mols of yellow phosphorus, $P_4=2P_2$, is relatively slower than the formation of the mols of red phosphorus. The condensation of red phosphorus from the vaporous state is independent of the presence of liquid yellow phosphorus. A. Stock and E. Stamm found that more red phosphorus is produced by chilling the vapour than corresponds with the dissociation into P_2-mols. The red phosphorus produced by chilling the vapour at 1200°, and 5 mm. press., does not contain more than one per cent. of yellow phosphorus. Hence, it is inferred (iv) that both P_2- and P_4-mols take part in the formation of red phosphorus, possibly in accord with the equation: $mP_2+nP_4=P_{2m+4n}$, which is a relatively faster reaction than $2P_2=P_4$. These results are in agreement with the observations of W. Marckwald and K. Helmholtz, who explain the phenomena observed by cooling liquid red phosphorus by assuming that the liquid contains both P_4-mols of yellow and P_n-mols of red phosphorus in equilibrium: $aP_4\rightleftharpoons bP_n$. Above the m.p. of red phosphorus, 592·5°, most of the mols are P_4, so that on rapid cooling the yellow variety is formed, but slow cooling allows a change of equilibrium in favour of the system on the right, and red phosphorus is deposited on solidification.

From observations on the effect of dissolved phosphorus on the vap. press. of carbon disulphide at 0°, G. Guglielmo concluded that the element is present in the form of P_4-mols; E. Beckmann, and A. Helff came to the same conclusion from ebulliscopic observations with the same solvent; and E. Paterno and R. Nasini, with benzene. J. Hertz obtained values in agreement with the presence of P_4-mols from observations on the effect of phosphorus on the f.p. of benzene. C. A. Seyler considered that the P_4-mol agrees best with the observed latent heat of fusion; E. Aston and W. Ramsay with the observed surface-tension of the molten liquid; and A. Smits and S. C. Bokhorst, with the critical constants. G. le Bas said that the mol. vol. of phosphorus does not agree with a 4-membered ring:



$$\begin{array}{c} P=P \\ P=P \end{array}$$

but is an agreement with a tetrahedron having a phosphorus atom at each corner—*i.e.* four 3-membered rings.

According to J. R. Rydberg,[4] the **hardness** of phosphorus is 0·5, when that of potassium is also 0·5; lead, 1·5: and copper, 3. C. A. Edwards gave 0·63 for the Brinell's hardness. J. Davy said that yellow phosphorus is brittle when cold, but of waxy consistency at ordinary temp. He added that it again becomes brittle at 34·33°, and it is then easy to pulverize. N. Slatowratsky and G. Tammann measured the **plasticity** of yellow phosphorus at various temp. up to the m.p., and found that a load of 55 kgrms. per sq. cm., sank into the material 2·5 units at 20°; 5·8 at 30°; 8·7 at 35°; 22·2 at 40°; and 79·0 at 43°—rather smaller values were obtained with a falling temp. G. Quincke, and R. Schiff measured the **capillary constants** of phosphorus. E. Aston and W. Ramsay found that molten phosphorus does not readily wet glass; they gave 43·09 dynes per cm. for the **surface tension** at 78·3° and 35·56 dynes per cm. at 132·1°; with the respective sp. gr. 1·714 and 1·664. These data give for the **molecular surface energy,** 748·2 and 629·6. T. W. Richards and co-workers [5] found the **compressibility** of yellow phosphorus to be $(\delta v/\delta p)/v=0{\cdot}0000199$ kgrm. per sq. cm., between 100 and 500 atm. 0·0000203 megabar, or 0·0000206 atm. at 20°; while the mean compressibility of red phosphorus between 100 and 500 atm. is 0·0000092 kgrm. per sq. cm., 0·0000290 megabar, or 0·0000091 atm. at 20°. The sparking which occurs when phosphorus is struck by a hammer is attributed by O. Ohmann to the evaporation of the element, and oxidation of the vapour.

According to H. Kopp,[6] the coeff. of **thermal expansion** of ordinary phosphorus from 0° up to its m.p. is quite regular, and its vol. at 44° is 1·017 times its vol. at 0°; when the solid melts, there is an abrupt expansion of 3·4 per cent., so that the vol. changes from 1·017 to 1·052. The vol. of the solid at $\theta°$ is $v=1{\cdot}05173+0{\cdot}000383\theta$; of the liquid, $v=1{\cdot}05173+0{\cdot}000532\theta$, or $v=1+0{\cdot}000506\theta$. G. Pisati and G. de Franchis gave for the solid at $\theta°$, when the vol. at 0° is v_0, $v=v_0(1+0{\cdot}0_3200\theta+0{\cdot}0_6115\theta^2)$; for the vol. of the liquid between 50° and 60°, $v=v_{50}\{1+0{\cdot}0_32969(\theta-50)+0{\cdot}0_62115(\theta-50)^2\}$. E. B. R. Prideaux gave $v=v_0(1+0{\cdot}000505\theta+0{\cdot}0_6118\theta^2)$ between 50° and 235°. Solid phosphorus has the mean coeff. of cubical expansion $0{\cdot}0_33674$; and the liquid, between 50° and 60°, $0{\cdot}0_3520$. A. Leduc gave for the coeff. of cubical expansion of the solid between 0° and the m.p., 0·000372; and for the liquid between 26° and 50°, 0·000560. G. Vincentini and M. Omodei gave 0·000520 for the solid, and 0·0005670 for the liquid; while A. Hess gave the respective numbers 0·000426 and 0·000595. The percentage expansion in passing from the solid to the liquid state was found by G. Vincentini and D. Omodei to be 3·5; G. Pisati and G. de Franchis gave 1·03446 for the vol. ratio of liquid and solid at 40°, and 1·0504 at 44°; and A. Leduc, 1·0345 at the m.p., 44·1°. H. F. Weibe studied the relation between the thermal expansion and the at. wt., b.p., m.p., and sp. ht.

H. Kopp [7] gave 0·202 for the **specific heat** of solid yellow phosphorus between 13° and 36°; C. C. Person, 0·212; and H. V. Regnault, 0·1895 between 7° and 13°; 0·1788 between −21° and 70°; and 0·1740 between −78° and 10°; and T. W. Richards and F. G. Jackson, 0·169 between −188° and 20°. For liquid phosphorus, C. C. Person gave 0·2045; P. Desains, 0·2; and A. Wigand, 0·202 between 13° and 36°. P. Nordmeyer gave 0·178 for the sp. ht. of yellow phosphorus between the temp. of liquid air and room temp. G. Schmidt gave 5·08 for the **atomic**

heat of solid yellow phosphorus, and 6·086 for gaseous phosphorus. D. H. Drummond gave for solid phosphorus $C_p=5{\cdot}30+0{\cdot}000341T$; and for liquid phosphorus $C_p=6{\cdot}10+0{\cdot}000341T$. W. A. Kurbatoff said that the at. ht. of phosphorus is lower than that of the metals, and the mols in the crystalline state are more complex than those of the metals. G. de Lucchi gave 1·175 for the mean ratio of the two sp. hts. of phosphorus vapour at 300°. The extreme values were 1·15 and 1·22. For solid red phosphorus, H. V. Regnault gave 0·16981–0·1705 between 15° and 98°; and A. Wigand, 0·1829 between 0° and 51°; 0·2121 between 0° and 134°; and 0·2162 between 0° and 199°. J. C. G. de Marignac found the sp. ht. of soln. of phosphorus in carbon disulphide $P+nCS_2$ to be 0·219 for $n=0{\cdot}25$; 0·222 for $n=0{\cdot}5$; 0·225 for $n=1$; 0·229 for $n=2$; and 0·2295 for $n=4$.

The **melting point** of ordinary phosphorus given by J. Davy[8] is 44·5°; P. Heinrich gave 46·25°; G. Quincke, 43°; H. M. Vernon, 45·3°; A. Smits and H. L. de Leeuw, and H. Kopp, 44°; A. Stock and E. Stamm, and A. Leduc, 44·1°; P. Desains, G. A. Hulett, C. C. Person, and A. Helff gave 44·2°; S. Lussana, 44·27°; A. Schrötter, 44·3°; and G. Pisati and G. de Franchis, G. Vicentini and D. Omodei, and A. Hess, 44·4°–44·5°. J. Böeseken obtained 44·77°, and claimed that the lower values have been obtained with imperfectly dried samples. Phosphorus which has been kept many days in vacuo still retains some adsorbed water. F. Scriba described an experiment in which a layer of water was cautiously poured over some conc. sulphuric acid, and a piece of ordinary phosphorus dropped on the water. The phosphorus sinks in the water and floats on the acid, where it is melted by the heat of the reaction between the water and the acid. G. A. Hulett, and G. Tammann measured the effect of press. on the m.p. G. Tammann gave for the m.p., θ°, at a press. of p kgrms. per sq. cm., $\theta=43{\cdot}93+0{\cdot}0275p-0{\cdot}0_650p_2$, or

p . . .	1	232	578	956	1431	1872
Melting point .	43·90°	50·01°	59·85°	70·18°	81·79°	92·01°

A. Stock found that the m.p. of phosphorus depends on the rate of heating; and in contradistinction to A. Smits and H. L. de Leeuw, A. Stock and E. Stamm did not find the m.p. of yellow phosphorus to be altered by heating it to 100° followed by rapid cooling. Molten phosphorus is easily obtained as an under-cooled liquid, even at temp. 40° below its m.p. A. Bellani, and H. Rose noted that contact with solid phosphorus causes an immediate solidification of the under-cooled liquid. The phenomenon is particularly marked with phosphorus which has been boiled under an aq. or alcoholic soln. of potassium hydroxide. Observations on this subject were made by T. de Grotthus, J. B. Kallhofert, A. Schrötter, F. P. Venable and A. W. Belden, P. Heinrich, J. W. Retgers, and D. Gernez. The last-named also measured the velocity of crystallization of the under-cooled liquid—*vide supra.*

When red phosphorus is warmed, said A. Schrötter, it becomes dark violet, but it does not melt, although W. Hittorf observed that the particles sinter together when it is heated in an evacuated sealed glass tube. H. Arctowsky said that when kept for 48 hrs. under a press. of 14–16 mm., red phosphorus forms microscopic crystals. Red phosphorus passes into ordinary phosphorus when heated. W. Hittorf said that the change does not occur at 324°, but the yellow phosphorus appears at 358°. A. Pedler observed no reaction when red phosphorus is heated in mercury vapour, but at a high temp., an inflammable vapour is given off without any signs of the residue changing. D. L. Chapman melted red phosphorus at 630° in a sealed tube and ordinary phosphorus was produced. A. Stock and co-workers found that in a sealed tube red phosphorus begins to sinter between 600° and 605°, and at 610° melts to a yellow liquid, while W. Hittorf's phosphorus melts at 620°. P. Jolibois gave 725° for the m.p. of red phosphorus in a sealed tube, and said that red phosphorus is stable between 450° and 610°. W. Marckwald and K. Helmholtz gave 592·5°±0·5° for the m.p. of red phosphorus, and A. Stock said that the m.p. depends on the rate of heating. W. A. Wahl observed that red phosphorus becomes black at 500°, and when confined in a capillary tube, it forms a yellow mobile liquid at 600°; on cooling, the colour deepens to a reddish-brown until solidification occurs. M. Volmer and I. Estermann observed that the fraction a of vaporized phosphorus which is condensed on a cold surface, while $1-a$ is reflected, varies between 0·2 and 0·5.

A. Smits and S. C. Bokhorst gave 589·5° at 43·1 atm. for the **triple point** of violet phosphorus. D. L. Chapman, and P. Jolibois estimated the triple point to be *c.* 600°. W. Marckwald and K. Helmholtz found the **transition point** of red to black phosphorus to be 575°. P. W. Bridgman found that the transition point of cubic or α-yellow phosphorus to hexagonal or β-yellow phosphorus to be:

p	1	6000	8000	10,000	12,000 kgrms. per sq. mm.
Transition point .	−76·9°	−2·4°	21·4°	43·7°	64·4°

R. Lorenz and W. Herz studied some relations of the transition temp. A. Smits and S. C. Bokhorst gave 690·9° for the **sublimation point** of violet phosphorus. C. Zengelis observed signs of the volatilization of red phosphorus at ordinary temp. According to B. Pelletier, the **boiling point** is 290°; J. Dalton gave 288°; E. Mitscherlich, 260°; P. Heinrich, 250°; G. Preuner and I. Brockmöller, 290° at 770 mm.; and G. Pisati and G. de Franchis, 278·3° at 762 mm. A. Smits and S. C. Bokhorst gave 265·5° at 562 mm.; 280·5° at 760 mm.; and 298·46° at 1048 mm.; while P. Jolibois gave 262° at 536 mm.; 281° at 786 mm.; and 295° at 1010 mm. According to A. Schrötter, the b.p. at different press., *p* mm., are:

p	120	173	204	266	339	393	514	760
Boiling point .	165°	170°	180°	200°	209°	226°	230°	287·3°

N. Blondlot found that ordinary phosphorus slowly sublimes at 40°; according to B. Pelletier, the vapour is colourless. The vapour of phosphorus is given off when phosphorus is boiled under water, and the luminosity produced in the condenser furnished E. Mitscherlich with a means of detecting phosphorus. The element also vaporizes slowly at ordinary temp. J. Joubert found the **vapour pressure** of solid yellow phosphorus at 5° to be 0·03 mm., and at 40°, 0·50 mm. M. Centnerszwer gave 0·0253 mm. for the vap. press of solid at 20°; 0·0724 mm. at 30°; 0·0893 mm. at 35°; and 0·1221 mm. at 40°. D. MacRae and C. C. van Voorhis represent these results by $\log_{10} p = 9·6511 - 3297·1T^{-1}$ mm. These investigators found the vap. press., *p* mm., of liquid yellow phosphorus from 44° to 150°; G. Preunier and I. Brockmöller, from 200° to 290°; and A. Smits and S. C. Bokhorst, from 210° to 581°:

	44·1°	69·92°	100·11°	150°	250°	280·5°	331·8°	504°	581°
p . . .	0·173	0·823	3·66	27·20	426	760	1877·2	17532	31236

D. MacCrae and C. C. van Voorhis represented their measurements between 44·1° and 150° by $\log_{10} p = 7·9542 - 2757·5T^{-1}$ mm. L. Troost and P. Hautefeuille measured the vap. press. of liquid yellow phosphorus between 360° and 510°, and found that above 510°, the liquid was transformed so rapidly into red phosphorus that its vap. press. could not be measured. They also measured the vap. press. of red phosphorus between 360° and 577°. E. Riecke represented their values for solid red phosphorus by $\log_{10} p = -45·01 + 16·28 \log_{10} T - 832T^{-1}$ atm.; and for liquid phosphorus, $\log_{10} p = -2·450 + 2·064 \log_{10} T - 1530\ T^{-1}$ atm. P. Jolibois also measured the vap. press. of red and yellow phosphorus. A. Smits and S. C. Bokhorst gave for solid and liquid violet phosphorus from 308·5° to the critical temp., 695°:

	308·5°	379·5°	486·5°	589·5°	593°	634°	695°
p . . .	0·07	0·35	5·46	43·1	44·2	58·6	82·2 atm.
		Solid.		M.p.	Liquid.		

They represented their results by $\log_{10} p = 19·2189 - 3585·96T^{-1} - 3·59 \log_{10} T$ mm.; and on the assumption, rendered probable by the work of L. Troost and P. Hautefeuille, and A. Smits and co-workers, that under-cooled liquid violet phosphorus and liquid yellow phosphorus are identical, D. MacRae and C. C. van Voorhis represented the vap. press. of liquid violet and yellow phosphorus from 145° to 634° by $\log_{10} p=11\cdot5694-2898\cdot1T^{-1}-1\cdot2566 \log_{10} T$ mm. In the vap. press. formula $-\log(p/p_c)=f(T_c/T^{-1})$, A. Smits and S. C. Bokhorst found that $f=3\cdot11$, between 200°–300°; 2·84, between 300°–400°; 2·60, between 400°–500°; and 2·40, between 500°–600°. A. Smits and co-workers found the vap. press. of black phosphorus to be rather less than that of violet phosphorus below *c.* 560°; about the same at 560°; and above that temp., the vap. press. is rather higher than that of violet phosphorus. Thus:

		515°	553°	567°	568°
Vap. press.	Black . .	8·5+	19·3+	28·6	39·5 atm.
	Violet . .	10·5	21·5	28·5	35·0 ,,

It is assumed that violet phosphorus is the stable form; but the metastable state of the element should have a higher vap. press. than the stable state, hence, it is further assumed that the mols. of the black and violet forms of phosphorus are not built up of the same kind of molecules. M. Centnerszwer found the partial press. of phosphorus vapour at 20° in an atm. of hydrogen is 0·0253 mm.; oxygen, 0·0251 mm.; carbon dioxide, 0·0312 mm.; coal-gas, 0·0242 mm.; air and iodobenzene, 0·0253 mm. W. Herz found that the constant c in the equation $\theta_1/\theta_2 = T_1/T_2+c(T_2-T_1)$ varies from 0·001374 to 0·001990. θ_1 and θ_2 denote the b.p. of two liquids at any press., and T_1 and T_2, the b.p. of the same liquids at another press.

W. Marckwald and K. Helmholtz found the **critical temperature** of yellow phosphorus to be 720·6°; J. J. van Laar gave 675° for the critical temp., and 80 atm. for the **critical pressure.** W. A. Wahl gave 695° for the critical temp. of violet phosphorus; and A. Smits and S. C. Bokhorst gave 82·2 atm. for the critical press. C. C. Person[9] found the **heat of fusion** of yellow phosphorus to be 4·71 to 5·2 cals. per gram at 44·2°; P. Desains gave 5·06 to 5·4 cals. per gram; and O. Pettersson, 4·74 cals. per gram, or, 0·15 cal. per gram-atom, at 29·73°; and 4·97 cals. per gram, or 0·15 cal. per gram-atom at 40·05°. G. Tammann gave for the heat of fusion, L Cals. per gram, at the following temp. and press. in kgrms. per sq. cm., 50·03° and 220, $L=4\cdot94$; at 69·98° and 959, $L=5\cdot28$ Cals.; at 90·21° and 1720, $L=5\cdot26$ Cals.; and at 100·18°, and 2155, $L=5\cdot19$ Cals. P. W. Bridgman found for the latent heat of fusion of phosphorus, L kilogrammetres per gram; the change of energy, δE; the change in vol., δv c.c. per gram; and the temp. θ, at a press. p kgrms. per sq. cm.:

	Yellow phosphorus.				Black phosphorus.			
p .	1	2000	4000	6000	6000	8000	10,000	12,000
θ .	44·2°	99·3°	148·2°	191·9°	−2·4°	21·4°	43·7°	64·4°
δv .	0·01927	0·91667	0·01436	0·01218	0·00851	0·00799	0·00746	0·00694
L .	2·09	2·41	2·63	2·78	18·61	20·24	21·82	23·29
δE .	2·09	2·07	2·06	2·4	18·10	19·61	21·06	22·44

A. Smits and co-workers calculated 10·2 Cals. for the molar heat of fusion of violet phosphorus. C. A. Seyler employed the heat of fusion and the sp. gr. of solid and liquid at the m.p. to calculate the number of atoms in the mol. R. de Forcrand, for the **heat of vaporization** of yellow phosphorus, gave 130·4 cals. per gram, or 4 Cals. per gram-atom, at 287°; and H. Giran obtained 3·89 Cal. per gram-atom for yellow phosphorus, and 7·60 Cals. per gram-atom for red phosphorus. A. Smits and co-workers calculated 12·5 Cals. for the heat of vaporization of liquid phosphorus at its b.p., 280°. A. Henglein gave 1·956 Cals. for the mol. heat of evaporation of phosphorus. The subject was studied by K. Bennewitz. This gives the normal value 22 for **Trouton's constant;** but the **heat of sublimation** of violet phosphorus is 25·8 Cals., and this gives the abnormally high value 37·5 for Trouton's constant. R. de Forcrand calculated values for the heats of fusion and vaporization of phosphorus. G. N. Lewis and co-workers calculate the **entropy** of gaseous phosphorus at 25° and 760 mm. press. to be 35·95 units per gram. D. H. Drummond gave $-70-0\cdot8T\log T+4\cdot87T$ cals. for the free energy of fusion, *i.e.* 13·1 cals. at 25°; and $58\cdot871+15\cdot4T\log T+0\cdot00033T^2-0\cdot0_68T^3-203\cdot7T$ for the free energy of vaporization, *i.e.* 6063 cals. per gram-atom at 25°. The entropy change on fusion is 0·506 cal., and on vaporization 25·5 cals. Hence, from G. N. Lewis and co-workers' value for phosphorus gas, the entropy of phosphorus at 25° is 9·95 units. E. Kordes discussed the changes of entropy on melting phosphorus. For the **heat of dissociation** $P_4=2P_2$, A. Stock and co-workers gave 49·2 to —50·3 Cals. H. Giran gave 4·4 cals. for the **heat of transformation** of white to violet phosphorus.

E. Petersen estimated the difference in the **heat of oxidation** of yellow and of red phosphorus to be less than 100 cals. T. Andrews gave 5747 cals. for the **heat of combustion** of a gram of ordinary phosphorus with oxygen; 4509 cals. per gram of oxygen; or 6479 cals. per litre of oxygen. P. A. Favre and J. T. Silbermann gave 209,476 cals. for the heat of oxidation of yellow phosphorus and 181,230 cals. for red phosphorus. H. Giran gave (2P,5O)=369·4 Cals. for yellow phosphorus, and 365·7 Cals. for the red form. J. J. B. Abria gave 351·48 Cals., and T. Andrews, 356·31 Cals. for yellow phosphorus. L. Troost and P. Hautefeuille found that commercial red phosphorus has a heat of combustion 362·82 Cals. and for samples of red phosphorus prepared at 265°, 360°, and 580° the heats of combustion have the respective values of 367·34, 345·34, and 362·86 Cals. The heat of combustion of ordinary yellow phosphorus is 369·90 Cals. J. C. Thomlinson has made some speculations on the relations between these values and the valency of the phosphorus atom; but the data on which the arguments are based apply to heterogeneous mixtures and not to a definite chemical individual.

The **index of refraction** of solid yellow phosphorus in air at 29·2° was found by B. C. Damien[10] to be 1·8244 for the *D*-line, 2·09300 for the H_α-line, and 2·19885 for the H_γ-line; and at 37·5°, 1·8191 for the *D*-line, 2·08873 for the H_α-line, and 2·19462 for the H_γ-line. He also found for liquid yellow phosphorus in air at 44°, 2·15274 for the *D*-line, 2·11311 for the *F*-line, and 2·05010 for the *C*-line; and at 55·3°, 2·14012 for the *D*-line, 2·09943 for the *F*-line, and 2·03754 for the *C*-line. He also found for the temp. coeff. $d\mu/d\theta$, —0·000051 per degree. J. W. Retgers gave 2·14 for the index of refraction of solid yellow phosphorus. E. Schmidt made some observations on this subject. F. P. le Roux gave 1·001364 for the index of refraction of phosphorus vapour; and C. Cuthbertson and E. P. Metcalfe, 1·001197 for light of wave-length $\lambda=589\cdot3\mu\mu$. They represented their results by $\mu-1=0\cdot001162(1+1\cdot53\times10^{-10}\lambda^{-2})$; and C. and M. Cuthbertson by $76\times10^{27}/(6534\times10^{27}-n^2)$. J. W. Retgers said that the crystals of red phosphorus have a high index of refraction. V. Berghoff found for *D*-light, at 20°, the refraction constants of soln. with 4·762, 13·043, and 20 per cent., *p*, of phosphorus in carbon disulphide, the respective values 0·002761, 0·002929, and 0·002975 for $(\mu-\mu_0)/p$; and H. G. Madan, for a sat. soln. of phosphorus in methylene iodide at 18°, 2·021, 1·984, 1·944, and 1·929 respectively for *G*-, *F*-, *D*-, and *C*-light. A. Haagen gave 0·4816 for the **specific refractory power,** and J. H. Gladstone, 0·590; A. Schrauf gave for the **refraction equivalent,** 0·019406 for phosphorus vapour in red-light —when the value for hydrogen is 0·00405—and 0·075547 for liquid phosphorus; and with the μ-formula, 0·000626 for the vapour, and 0·002437 for the solid. J. H. Gladstone gave 18·3 for the refraction equivalent—when the value for hydrogen is unity—and he also gave 3·0 for the **dispersion equivalent.** F. Zecchini showed that the **atomic refraction** of phosphorus changes with the nature and number of other elements with which it is combined. For temp. ranging from 18·6° to 29·3°, he found for the at. refraction of phosphorus in

	$P(C_2H_5)_3$	$P(C_2H_5)_4I$	PCl_5	$POCl_3$	PBr_3	P_2I_4	$P(C_6H_5)_3$
μ-formula . .	17·24	18·24	16·65	8·92	20·01	24·12	24·34
μ^2-formula . .	9·47	10·29	8·81	4·92	9·72	9·92	11·18

The at. refraction is least in the chlorides of phosphorus and greatest in the iodide, the value deduced from the bromide being intermediate. Hydrogen phosphide gives a much lower value for the at. refraction of phosphorus than do the halogen compounds of the same type. Compounds of phosphorus with the same elements give practically the same values for the at. refraction; this is especially well shown with the tri- and penta-chlorides. The very low refraction eq. of phosphorus oxychloride is remarkable; it gives the at. refraction of phosphorus as less than half that which the element has in the free state or when combined with chlorine alone. The μ-formula gave more consistent results than the μ^2-formula; and the values were greater with the D-ray than with the H_α-ray. W. A. Kowalewsky found 7·71 for the at. refraction of phosphorus in the chloroanhydrides of alkyl phosphates. C. P. Smyth studied this subject; and J. E. Calthrop, the relation between the at. vol. and the index of refraction.

J. Kerr found phosphorus to have a positive double refraction in the electric field. K. Schultz-Sellack showed that an 8-mm. layer of a soln. of 10 parts of phosphorus in one of carbon disulphide absorbs 52 per cent. of the rays emitted from a lampblack surface at 100°; and 57 per cent. of the heat rays from a coal-gas flame.

R. T. Simmler[11] showed that the **flame spectrum** of burning phosphorus is continuous. Burning phosphine gives no line spectrum; and phosphoric acid colours the non-luminous gas-flame blue. J. Plücker observed that the ordinary electric discharge tube filled with hydrogen and phosphorus vapour shows only the spectrum of hydrogen, but with the vapour of phosphorus trichloride he observed lines due both to chlorine and to phosphorus. When phosphorus is introduced into a flame, the inner cone is coloured green; and if hydrogen be passed over phosphorus, or, according to L. Dusart, if phosphorus, hypophosphorous, or phosphorus acids or their salts be introduced into an apparatus generating hydrogen, the gas subsequently burns with an emerald-green flame, and a yellowish-red film is deposited on a piece of cold porcelain held in the flame. The presence of alcohol, ether, or of several organic substances retards the action. The spectrum of a hydrogen flame containing phosphorus shows two green lines, one of which is close to the green barium line. J. Plücker and J. W. Hittorf first obtained the **line spectrum** of phosphorus from a warm evacuated discharge tube containing a little phosphorus. The line spectrum was also observed by G. Salet, A. Ditte, K. B. Hofmann, A. de Gramont, E. Demarçay, A. E. Ruark and co-workers, F. Exner and E. Haschek, A. Hagenbach and H. Konen, P. Geuter, E. Goldstein, and J. M. Eder and E. Valenta. The more important lines are 6506 in the red; 6058 and 6033 in the orange-yellow; 5421, 5403, 5382, 5338, 5307, 5285, and 5244 in the green; 4601 and 4589 in the blue—Fig. 7. M. Curie studied the spark spectrum of liquid phosphorus; and A. de Gramont, the ultimate lines of the spectrum. The **band spectrum** of phosphorus was considered by J. Formanek to be best observed in the flame of burning hydrogen obtained by putting a very small piece of phosphorus in an apparatus generating hydrogen gas. The inner cone appears green. The spectrum shows four bands—a feeble one in the orange-yellow, about 5995; a pale yellowish-green band about 5606; a pale greenish yellow band about 5264; and a feeble green band about 5107—Fig. 8. J. E. Purvis found that the vapour shows no absorption bands in the ultra-violet. G. Salet showed

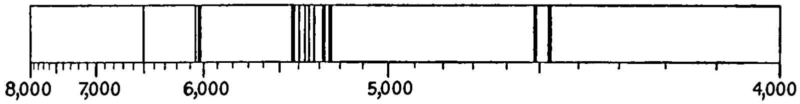


FIG. 7.—The Line Spectrum of Phosphorus.

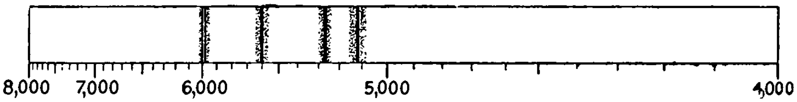


FIG. 8.—The Band Spectrum of Phosphorus.

that this procedure is a very sensitive means of detecting phosphorus in iron, or in cases of phosphorus poisoning. The banded flame spectrum was examined by J. M. Séguin, P. Christofle and F. Beilstein, A. Petrikaln, E. Mulder, A. Mitscherlich, O. S. Duffendack and H. Huthsteiner, W. N. Hartley, F. Exner and E. Haschek, and P. Geuter. The band spectrum was also investigated by G. Salet, L. de Boisbaudran, C. J. Lundström, W. N. Hartley, C. de Watteville, and A. de Gramont and C. de Watteville. The **arc spectrum** was studied by H. Kayser and C. Runge, F. Exner and E. Haschek, M. O. Saltmarsh, A. Hagenbach and H. Konen, and J. M. Eder and E. Valenta. The absorption spectrum was described by J. N. Lockyer; and the emission spectrum of the heated vapour by E. Paterno and A. Mazzuchelli. The effect of *temperature* was examined by G. Ciamician, and A. Schuster; and these investigators also examined the effect of *pressure*. A. de Gramont studied the action of the so-called *self-induction* on the spectrum of phosphorus compounds. R. A. Millikan and I. S. Bowen studied the extreme ultra-violet spectrum. W. W. Shaver measured the spectral lines produced by the electrodeless discharge in phosphorus vapour; F. Holweck, the ultra-violet spectrum; C. R. Crymble, the absorption spectrum of the phosphorus chlorides; and J. J. Dobbie and J. J. Fox, the absorption of light by the vapour of phosphorus. A. Petrikaln, W. Centnerszwer and A. Petrikaln, W. N. Hartley, and H. J. Emeléus and R. H. Purcell discussed the origin of the ultra-violet spectrum of glowing phosphorus; and the last-named concluded that it has its origin in the molecule of an oxide. According to A. Fowler, and W. M. Hicks, no **series spectral lines** have been observed in the phosphorus spectrum; but M. O. Saltmarsh found that the series system in the spectrum of doubly ionized phosphorus is a doublet system in accordance with the spectroscopic displacement law. Three members of the triplet series of the spectrum of trebly ionized phosphorus have been identified. For three groups of elements, each having its own characteristic electron structure, the sharp terms are greater than the diffuse terms with the same Rydberg's number for the neutral and singly ionized element, but for higher stages of ionization the diffuse terms are greater than the sharp. R. B. Lindsay, O. Laporte, N. K. Sur, J. C. McLennan and A. B. McLay, I. S. Bowen, and R. A. Millikan and I. S. Bowen discussed this subject. The general subject was reviewed by H. Kayser. W. W. Coblentz measured the **ultra-red transmission spectrum** of phosphorus. M. Centnerszwer, and A. Petrikaln found the luminous glow of phosphorus in an organic solvent has a continuous spectrum in the visible region, but in the ultra-violet there are fourteen sharp lines and a band near 3252. A. Petrikaln found broad bands covering the fourteen lines between $\lambda=2381$ A. and 2613 A. previously observed. H. J. Emeleus and W. E. Downey did not agree with the latter conclusion. They also found that when phosphorus burns in enriched air with a flame temp. of 800°, there are five bands in the ultra-violet at $\lambda=2390$, 2475, 2530, 3630, and 3275 A.; the same bands occur when phosphorus burns under reduced press. with a flame temp. of 125°, but the bands are resolved into smaller bands; and when phosphorus glows, it emits the same bands as the low temp. flame. H. J. Emeléus found the same spectrum is emitted from glowing phosphorus oxide, and phosphine burning in oxygen. E. Schmidt said that phosphorus is opaque to the ultraviolet rays.

The K-series of the **X-ray spectrum** was examined by H. Fricke,[12] J. Bergengren, M. de Broglie and A. Dauvillier, E. Bäcklin, O. Stelling, D. M. Bose, F. L. Mohler and P. D. Foote, G. Wentzel, E. Hjalmar, O. Lundquist, L. A. Turner, A. E. Lindh, C. D. and D. Cooksey, G. Wentzel. S. K. Allison, F. Holweck, J. C. McLennan and M. L. Clark, studied the L-series of the X-ray spectrum. A. Dauvillier could not find the L_α-ray. According to J. Bergengren, the wave-lengths of the limits of absorption in the X-ray absorption spectra of the different varieties of phosphorus, are different for black phosphorus and for phosphorus in the form of phosphoric acid; that of red phosphorus shows a double limit, one component of which is identical with that of black phosphorus, and the other, attributed to yellow phosphorus, coincides, at least approximately, with that of phosphoric acid. T. E. Aurén found the relative at. absorption coeff. of phosphorus for X-rays is 5·68 when that of lead is 569. O. Stelling studied the effect of radicles bound directly to quinquevalent phosphorus on the *K*-absorption wave-lengths, and also the effect of different valencies of phosphorus with the same radicles. Elements bound directly to quinquevalent phosphorus cause a shift of the *K*-absorption towards a longer wave-length in the order $O<N<H<C<Cl$. These results were discussed by S. Aoyama and co-workers, and M. de Broglie and A. Dauvillier. F. L. Mohler and P. D. Foote[13] gave 5·80 volts for the **resonance potential** of phosphorus vapour, and 13·3 volts for the **ionization potential.** A. E. Ruark and co-workers gave 13·3 volts for the ionization potential and 5·80 volts for the inelastic **collision potential.** K. T. Compton discussed this subject. O. S. Duffendack and H. Huthsteiner gave 10·3 volts for the **arcing potential** of the vapour of red phosphorus at 335°, and they regard this as the ionizing potential of the phosphorus atom. J. E. P. Wagstaff calculated the **vibration frequency** of red phosphorus to be $6·3\times10^{-12}$, and M. Holweck gave 128 volts for the critical potential of the *L*-series of the X-ray spectra. R. N. Ghosh discussed the relation between the ionizing potential and the electronic structure; and S. C. Biswas, and the mol. vol.

The **actinic properties** of the light from burning phosphorus were found by J. M. Eder[14] to be much less than those of burning magnesium or aluminium. The actinic properties of the flame obtained when a soln. of phosphorus in carbon disulphide is burnt, were mentioned by J. Murray. L. Rolla and G. Piccardi studied the ionization of phosphorus in flames.

According to M. Faraday,[15] liquid and solid yellow phosphorus are non-conductors of electricity; G. L. Knox said that the **electrical conductivity** of fused phosphorus is small; A. Matthiessen observed that if the conductivity of silver be 100 at 0°, then that of red and yellow phosphorus is $0·0_5123$ at 20°; and G. Foussereau gave $0·957\times10^{-11}$ mho for the conductivity of solid phosphorus at 11°, and $0·641\times10^{-10}$ mho at 42°, while for liquid phosphorus, he obtained $0·435\times10^{-6}$ mho at 25°, and $0·289\times10^{-5}$ mho at 100°. P. W. Bridgman found the electrical resistances, *R*, of black phosphorus at different temp. and press., *p*, in kgrms. per sq. cm., were:

p . . .		0	3000	6000	9000	10,000	12,000
R	0° . .	1·000	0·492	0·2042	0·0783	0·0565	0·0297
	50° . .	0·662	0·313	0·1371	0·0572	0·0427	0·0238
	100° . .	0·421	0·195	0·0910	0·0425	0·0337	0·0209

The average value of the press. coeff. is —0·000293 at 0° between 0 and 12,000 kgrms. per sq. cm. press.; —0·000277 at 50°; and —0·000250 at 100°; and for the temp. coeff., at 0° the temp. coeff. is —0·000200, and at 12,000 kgrms. per sq. cm. press., —0·000320; the corresponding values at 50° are —0·000231 and —0·000290 respectively; and at 100°, respectively —0·000262, and —0·000249. The sp. resistance was 1000 ohms per cm. cube at 0°. W. R. Grove found that phosphine is formed when a current is passed through ordinary molten phosphorus, but if the occluded gases have been previously expelled by heating the phosphorus in vacuo, no phosphine is formed. P. Walden found that a soln. of phosphorus in phosphorus trichloride is a non-conductor. O. Reichenheim discussed the conductivity of phosphorus vapour. The action of an electrical discharge on phosphorus vapour has been discussed in connection with red phosphorus. O. W. Richardson found that phosphorus vapour discharges a hot positively charged platinum plate, and the vapour is probably adsorbed by the metal. The effect is not due to the oxidation of phosphorus, because, as indicated below, both positive and negative ions are then present. A. Günther-Schulze discussed the conductivity of phosphorus; and K. F. Herzfeld discussed the relation between the refractive index and the conductivity. K. Przibram examined the conductivity of the fumes from phosphorus. P. W. Bridgman found the **thermoelectric force** of black phosphorus and copper from 0° to 21° is 0·000413 volt per degree, a positive current flowing from the copper to the phosphorus at the hot junction. A. Matthiessen found the thermoelectric power of red phosphorus and lead to be 29·9 microvolts. A. Avogadro studied the position of phosphorus in the **electrochemical series**; it probably comes between fluorine and carbon. F. W. Bergstrom found the electrochemical series in liquid ammonia: Pb, Bi, Sn, Sb, As, **P**, Te, Se, S, I. M. le Blanc and D. Reichenstein measured the electrode potential of phosphorus in soln. of potassium hydroxide, and sulphuric acid. R. Schenck found the **potential difference** of the hydrogen-phosphorus couple to be 0·168 volt at 13·6°, so that the phosphorus electrode is negative to that of hydrogen. W. Beetz studied the gas-cell with phosphorus vapour, and platinum with occluded hydrogen; O. S. Duffendack and H. Huthsteiner, the low voltage arc in phosphorus vapour. W. Busse measured the distribution of the sizes of the ions in phosphorus vapour and found that there is a continuous gradation from the largest to the smallest.

According to M. Faraday,[16] phosphorus is diamagnetic; and the subject was examined by J. Plücker, F. C. O. von Feilitzsch, J. Tyndall, F. Zantedeschi, and E. Becquerel. G. Quincke gave for the **magnetic susceptibility** of yellow phosphorus at the m.p., $-1{\cdot}6\times10^{-6}$ vol. units; P. Curie, $-0{\cdot}92\times10^{-6}$ mass units at 19°–71°; P. Pascal, $-0{\cdot}884\times10^{-6}$ mass units; and K. Honda, $-0{\cdot}88\times10^{-6}$ mass units at 18°. For red phosphorus, S. Meyer gave $-0{\cdot}23\times10^{-6}$ mass units at 18°; and P. Curie, $0{\cdot}73\times10^{-6}$ mass units at 20°–275°. P. Pascal gave -274×10^{-7} for the at. magnetization of yellow phosphorus. K. Honda studied the thermomagnetic properties of yellow phosphorus. P. Pascal compared the magnetic susceptibilities of the elements of the family group, and found the logarithm of the susceptibility to be a linear function of the at. wt. H. Schlundt gave for the **dielectric constant** of solid yellow phosphorus, 4·1 at 20°, and for liquid phosphorus, 3·85 at 45°. G. L. Addenbrooke studied the relation between the dielectric constant and the physical properties; and J. H. Jones, the relation between the dielectric constant and the electronic structure. B. H. Wilsdon studied the subject.

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§ 6. The Oxidation of Phosphorus

M. van Marum,[1] A. van Bemmelen, and B. Meijlink showed that the oxidation of phosphorus is accelerated if the air is rarefied, and when the phosphorus is at the same time covered with cotton, or powdered resin or sulphur, the phosphorus ignites at the ordinary temp. A. D. Bache said that the phosphorus can be ignited even without these powders, but that the powders—charcoal, boric acid, potassium or barium hydroxide, lime, calcium carbonate, magnesia, ammonium, sodium or calcium chloride, nitre, fluorspar, silica, arsenic, antimony, manganese, etc.—do facilitate the inflammation. Animal charcoal and lampblack are specially favourable, so that phosphorus sprinkled with charcoal ignites at 15·5° in the open air. When yellow phosphorus burns in a limited supply of air, there may be produced a suboxide, corresponding with that described by U. J. J. Leverrier, as well as phosphorus trioxide, phosphorus tetroxide, phosphorus pentoxide, along with some red phosphorus. R. Cowper and V. B. Lewes showed that the product may contain some unchanged yellow phosphorus. When the products of combustion are treated with water, phosphoric, phosphorous, and hypophosphorous acids as well as phosphine may be formed as indicated more particularly in connection with these compounds. U. J. J. Leverrier showed that if water be gradually added to the products of combustion, there is formed a golden-yellow liquid which coagulates at 80°; and if water in excess be added, a colourless soln. and a red precipitate are formed. B. Reinitzer considers that the reaction can be in part represented by $5P_2O_3=3P_2O_5+P_4$. The golden-yellow soln. contains a colloidal substance $mP_2O_3.nH_2O$, which is not phosphorus anhydride, because the aq. soln. is neutral. The red precipitate is considered to be a solid hydride $(P_4H_2)_n$, with more or less hydrogen replaced by oxygen. T. E. Thorpe and A. E. H. Tutton could not confirm these observations.

When yellow phosphorus burns in an excess of oxygen, the main product is phosphorus pentoxide—possibly mixed with a little red phosphorus. When a considerable quantity of air is passed over phosphorus, the slow combustion which first occurs produces a slight elevation of temp. which gradually accelerates the reaction, until finally the phosphorus bursts into flame. Anything which hinders the dissipation of the heat generated during the oxidation, or hastens the rate of oxidation, favours the ignition of the phosphorus at a low temp. Thus, L. Hünefeld found that if the phosphorus be wrapped in blotting paper, or even if a freshly cut surface be in contact with blotting paper, the phosphorus may fuse at the corners, or edges, and ignite at 20°. The discoverers of phosphorus must have noticed the white clouds which are formed when that substance is burned in air; and the product was mentioned by S. A. Frobenius, A. G. Hanckewitz, etc. Again, finely divided phosphorus may ignite in air after it is dried. According to W. A. Lampadius, filter-paper, or, as recommended by O. Ohmann, asbestos-paper, soaked with a soln. of phosphorus in carbon disulphide, ignites as the solvent evaporates and leaves the phosphorus in a fine state of subdivision on the paper—*vide infra*, action of carbon disulphide on phosphorus.

The old *phosphorus boxes* contained preparations which absorbed moisture from the air with the evolution of heat. The resulting rise of temp. favoured combustion. For example, the mixture of yellow and red phosphorus, and phosphoric and phosphorous oxides and acids, obtained by blowing a jet of air into a flask with some warmed phosphorus, may ignite when exposed to moist air. The phosphoric oxides keep the phosphorus in a fine state of subdivision. J. Pelouze obtained a luminous mixture by melting phosphorus with phosphoric oxide, or calcined magnesia, or lime. M. Saltzer melted phosphorus with about one-third its weight of wax; sent a jet of air into the flask until the phosphorus inflamed and then closed the flask. E. Benedix fused a mixture of powdered cork, beeswax, phosphorus, and naphtha. The mass fired spontaneously at 20°, or at a lower temp. if breathed upon.

J. Davy also showed that the inflammation of yellow phosphorus is favoured by the rarefaction of air, and retarded by compression. Thus phosphorus heated until it takes fire in a closed vessel, is soon extinguished by the press. produced by the heat. The flame reappears on opening the vessel. The inflammation temperature is so low that the heat of the body suffices to raise the temperature of the phosphorus above its kindling temperature, and hence phosphorus should always be "handled" with the forceps, never with the bare fingers unless under water. Burns produced by phosphorus are very painful, and heal very slowly. F. H. Eydmann measured the **ignition temperature** of phosphorus submerged in water whose temp. was gradually raised while a current of air or oxygen was bubbled through the fused mass. The ignition was assumed to occur when the temp. of the water increased very rapidly. This was found to be 45·0°–45·2° in air, oxygen, or air diluted with an equal vol. of carbon dioxide. The ignition temp. is thus independent of the conc. of the oxygen. According to F. Molnar, the ignition temp. of ordinary phosphorus in air containing ozone is 4° higher than in purified air; it is higher in dry air than in moist air, and this the more the greater the humidity of the air. Thus, phosphorus inflamed at 30° in air sat. with water vapour at 30·1°; and at 17° in air sat. with water vapour at 38·1°. It inflamed at 47° in air sat. with alcohol; at 82° in air sat. with ether; at 87° in air sat. with carbon disulphide; and at 18° in air sat. with turpentine vapour. Phosphorus at rest can be heated in air to 205° without ignition, but with a slight agitation, it ignites at 45°. H. Rebenstorff said that phosphorus ignites in 20 seconds if in contact with a clean strip of amalgamated aluminium. Numerous lecture experiments have been devised for demonstrating different phases of the combustion of phosphorus.

W. Hittorf [2] said that red phosphorus does not ignite in air at 255°; and A. Schrötter gave 260° for the ignition temp. in air, and H. B. Baker and H. B. Dixon gave 260° for the ignition temp. in moist oxygen. J. Personne observed that red phosphorus is slowly oxidized and acidified by exposure to air, and L. Guerri showed that phosphorous and metaphosphoric acids are produced—*vide infra*. C. F. Schönbein said that unlike ordinary phosphorus, red phosphorus does not ozonize air, and it does not vaporize at ordinary temp. Hence, red phosphorus is not luminescent in air. T. B. Groves said that moist red phosphorus may slowly oxidize in air, and produce ozone without being luminous. H. B. Baker and co-workers showed that neither yellow nor red phosphorus readily ignites in thoroughly dried oxygen.

In the seventeenth century, Robert Boyle was much impressed by the fact that a body like phosphorus was able " to shine in the dark without having been before illumined by any lucid substance, and without being hot as to sense " ; and by the remarkably small amount of phosphorus required to produce a luminous effect. He said :

> A grain of the noctiluca dissolved in alcohol of wine and shaken in water rendered 400,000 times its weight luminous throughout ; at another trial I found that it impregnated 500,000 times its weight ; which was more than one part of cochineal could communicate its colour to. And one thing further observable was that when it had been a long time exposed to the air, it emitted strong and odorous exhalations distinct from the visible fumes.

The strong and odorous exhalation described by R. Boyle is now called ozone. M. van Marum, J. B. de Mons, and J. Davy showed that when phosphorus is exposed to air at ordinary press. and a temp. above 7°, the slow oxidation is attended by a very slight rise of temp., and a pale greenish light visible only in darkness is emitted : at the same time white fumes with an unpleasant garlic-like odour are emitted. In 1681, F. Slare gave an account of one of the most paradoxical phenomena connected with the luminosity of phosphorus, for he showed that the glow is increased by rarefying the air. He said :

> It being now generally agreed that the fire and flame of phosphorus have their pabulum out of the air, I was willing to try this matter in vacuo. To effect this I placed a considerable lump of phosphorus under a glass, which I fixed to an engine for exhausting the air ; then presently working the engine, I found it to grow lighter (*i.e.* the phosphorus to become more luminous), though a charcoal that was well kindled would be quite extinguished at the first exhaustion ; and upon the third or fourth draught, which very well exhausted the glass, it much increased in light, and continued to shine with its increased light for a long time ; on re-admitting the air, it returns again to its former dulness.

The observation was confirmed by F. Hauksbee, and G. Homberg ; while J. Davy, working along the same line, said that in rarefied air, the luminosity increases with the degree of rarefaction, and that the light does not diminish in brightness under the reduced press. attained by the air-pump ; if air be then suddenly emitted, the light disappears. Phosphorus does not glow in vacuo, nor in air at 4 atms. press. C. G. von Helwig also found that in compressed air, phosphorus does not luminesce until the temp. is raised. Some discrepant results have been reported owing to the neglect of certain impurities in the gases employed. J. F. A. Göttling stated that phosphorus does not glow in oxygen prepared from mercuric oxide, but it becomes luminous in nitrogen ; J. B. de Mons, however, showed that the luminescence of phosphorus in nitrogen is due to the presence of traces of oxygen. J. Davy showed that phosphorus can be volatilized in oxygen at a temp. at which it does not luminesce, and luminosity occurs when nitrogen or hydrogen is introduced into the gas. J. Davy, and C. L. Berthollet found that if oxygen be excluded, phosphorus does not glow in inert gases—carbon dioxide, nitrogen, hydrogen, carbon monoxide, hydrogen chloride, etc. According to J. Davy, phosphorus does not glow in pure oxygen at temp. below 16° ; if the press. be increased to 1·5 atms., the glow does not appear until the phosphorus has been heated to its m.p., and then it takes fire ; phosphorescence occurs at ordinary temp. if the gas be slightly rarefied, or its partial press. be reduced by dilution with an inert gas. Hence, *at a given temp., a certain critical pressure of the oxygen is needed to start phosphorescence.* This press. is called by M. Centnerszwer the *Leuchtdruck* or *luminescence pressure.* According to J. S. C. Schweigger, the more oxygen is rarefied, either by diminishing the press., or by admixture with an inert gas, the lower the temp. at which the luminescence of phosphorus occurs. Consequently, at a given press. a certain *critical temperature*—P. Duhem's *le point de réaction*—is needed for the luminescence of phosphorus. P. Duhem considers the phenomenon to be a case of *le faux équilibre*, where the limiting or critical temp. at different press., obtained by J. Joubert, were:

	1·4°	3·0°	5·0°	8·9°	11·5°	14·2°	19·2°
p . .	355	387	428	519	580	650	760 mm.

When plotted, the curve, Fig. 9, divides the plane into two regions; the region above the curve represents systems where phosphorus is undergoing oxidation; and the region below where no oxidation is taking place, and he therefore calls it *le region des faux équilibres.* J. Chariton and Z. Walta also said that the oxidation is inappreciable below a definite critical press., but M. Bodenstein objected that the conclusion is a result of faulty measurements.

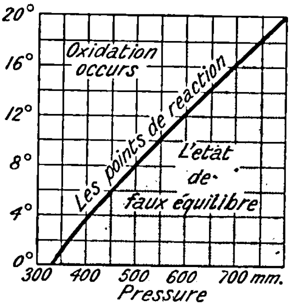

FIG. 9.—J. Joubert's Observations on the Oxidation of Phosphorus.

C. Barus thought that phosphorus actually emitted charged particles of an "emanation" which served as condensation nuclei for water vapour. These were presumably charged ions. W. P. Jorissen, H. E. Armstrong, and G. Bredig and W. Pemsel mention that an emanation from oxidizing phosphorus is able to penetrate opaque substances and affect a photographic plate; but M. Centnerszwer and A. Petrikaln found that the photographic effect is not produced if the products of oxidation are removed as fast as they are formed, and they attribute it to a volatile oxidation product—perhaps hydrogen dioxide. J. Elster and H. Geitel found that whatever be the emanation it is not able to produce an electrical effect on the other side of a quartz plate. A. Blanc observed that the oxidation of phosphorus in air is accompanied by an ionizing radiation of low penetrative power. W. P. Jorissen and W. E. Ringer did not observe any increase in the luminosity by exposing the oxygen to radium radiations, though the light from an electric arc accelerated the process.

At the end of the seventeenth century, R. Boyle noticed that phosphorus is luminous only in the presence of air; and in 1795, W. A. Lampadius showed that phosphorus does not luminesce in dry air. L. J. Thénard found that the slow oxidation of phosphorus ceases in the course of an hour when the air or oxygen is dry. L. Gmelin said that phosphorus does not fume in air dried over sulphuric acid, though it still luminesces feebly in the dark. J. Davy found phosphorus burns as rapidly in air dried by sulphuric acid, as it does in ordinary air. J. J. Berzelius, and E. Marchand inferred that the luminosity of phosphorus at low temp. is not altogether the result of oxidation, but is partly due to vaporization and a mol. change; this hypothesis, however, does not explain the retarding influence of those chemically inactive gases which prevent the oxidation, but not the vaporization of the phosphorus. The ideas of the early workers on the drying of gases are different from those which prevail to-day. H. B. Baker and co-workers showed that if moisture be rigorously excluded phosphorus does not oxidize in air or in oxygen, and no luminescence occurs. The experiments of E. Scharff, E. Mitscherlich, J. Joubert, A. Schrötter, G. Meissner, W. Müller-Erzbach, and E. J. Russell are also decisive in showing that the glow is the concomitant of a chemical process dependent on the presence of oxygen—no oxidation, no glow. H. P. Waran observed periodic flashes on admitting small bubbles of oxygen into a vessel containing phosphorus deposited on the walls by vaporization. E. Q. Adams calculated that the ratio of the production of light to the energy input in the case of phosphorus vapour in nitrogen in contact with air is slightly above one lumen per kilowatt at 25° or at 40°.

R. Boyle observed that the presence of a minute quantity of a number of essential oils—*e.g.* oil of mace or of aniseed—extinguished the glow of phosphorus. J. Davy, H. A. von Vogel, and T. Graham showed that the luminescence is not prevented when the vapour of sulphur, or of acetic acid, hydrogen chloride, or ammonia is present; phosphorus is luminous in hydrogen chloride or carbon dioxide when but a trace of oxygen is present. The luminosity is diminished or stopped by a small proportion of phosphine, hydrogen sulphide, sulphur doxide, carbon disulphide, iodine, chlorine, nitrous oxide, nitric oxide, methane, ethylene, ether, alcohol, naphtha, turpentine, camphor, creosote, and other volatile oils. Thus, T. Graham found that phosphorus is not luminous in air at 21° which contains 0·001 vol. of phosphine (not spontaneously inflammable in air); and H. A. von Vogel said that 0·83 vol. of sulphur dioxide will stop the luminosity of phosphorus in air at 10° but not at 18°; less than 0·001 vol. of turpentine vapour will also extinguish the glow. The effect of numerous other volatile organic substances was examined by M. H. Deschamps, J. Chappius, M. Centnerszwer, K. R. K. Iyer, and E. Scharff.

It is very curious to find that phosphorus will not glow in oxygen at ordinary atm. press. and temp., but if the oxygen be rarefied, the glow at once begins, and ceases immediately the oxygen is compressed. If the luminosity were simply an oxidization process, the converse might have been predicted. According to M. Centnerszwer, and E. J. Russell, luminosity or oxidation commences in moist oxygen when the gas has a partial press. of 500–600 mm., and with dry oxygen, according to T. Ewan, luminosity commences at 20° when the partial press. of this gas is 200 mm. E. J. Russell found a small amount of moisture is necessary for the oxidation of phosphorus by oxygen gas, and that the amount remaining in a gas after treatment with conc. sulphuric acid is most suited for rapid oxidation. W. Busse added that while the oxidation of phosphorus is greatly influenced by the presence of water vapour, and reaches a maximum when the moisture content is so regulated by conc. sulphuric acid that about 10^{14} to 10^{15} mols of water are present per c.c. Extreme drying, however, does retard the oxidation of phosphorus, but does not completely inhibit the process, so that whilst water is a catalyst for the oxidation, it is not essential. Dry phosphorus in the dark becomes coated with a film of oxide, so that a store of oxide accumulates. This undergoes a sudden oxidation to the pentoxide, accompanied by luminescence, when local changes of temp. occur. According to E. J. Russell, the oxidation occurs in two stages: First, a slow oxidation accompanied by a feeble glow, followed by a continuously accelerated process of oxidation when the glow is very bright. Phosphorus pentoxide seems to be formed in the second stage, and an unrecognized oxide in the first stage: R. Schenck and co-workers, L. and E. Bloch, E. Jungfleisch, E. Scharff, H. B. Weiser and A. Garrison, E. Gilchrist, C. C. Miller, and N. Blondlot assume this oxide to be phosphorus trioxide. Consequently, the first stage involves the oxidation of phosphorus to the trioxide without glow; and the second stage, the oxidation of the trioxide (*q.v.*) to the pentoxide with glow. When much moisture is present, the process of oxidation appears to be retarded, possibly owing to the formation of a protective film of moisture on the phosphorus. With moderately dried oxygen, too, measurements of the speed of oxidation are complicated by the formation of a film of oxide on the surface of the oxidizing phosphorus. With moist oxygen, the connection between the rate of oxidation and the press. of the gas is illustrated by the curve, Fig. 10, where the speed of the reaction, zero at 700 mm., increases rapidly as the press. falls, and then varies within narrow limits over press. ranging from about 500 mm. to about 100 mm., and finally decreases rapidly to zero, in vacuo. J. Chariton and Z. Walta found that there is a relation between the vap. press. of the phosphorus and the critical press. of the oxygen below which no oxidation occurs. The critical press. is lowered if argon be present. If the press. of the oxygen be below a *critical pressure*, no rapid reaction occurs. The value of the critical press. is greater the greater the press. of the phosphorus vap. Above the critical press., the reaction is extremely

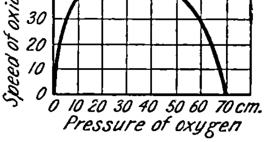

FIG. 10.—The Effect of Pressure on the Oxidation of Phosphorus.

rapid. If oxygen is admitted until its critical press. is nearly reached, and then argon is allowed to enter, the luminescence appears; the effect is as though the press. of the phosphorus had diminished, but the intensity of the light is less. With argon almost at atm. press., the glow made its appearance immediately oxygen was allowed to enter, but its intensity was very feeble. As shown by C. F. Schönbein, H. McLeod, C. T. Kingzett, J. Chappius, A. R. Leeds, etc., ozone and hydrogen dioxide are formed when the moisture is present in excess; these substances are not direct products of the reaction between phosphorus and oxygen. In addition, ammonium nitrate and nitrite, according to C. F. Schönbein, and E. J. Russell, are formed when the oxidation of the phosphorus is effected.

The work of W. Schmid, J. Corne, Lord Rayleigh, W. Müller-Erzbach, E. Scharff, J. Joubert, etc., makes it very probable that the luminosity is produced by the oxidation of the vapour of phosphorus. E. Jungfleisch said that the amount of phosphorus volatilized at ordinary temp. is too small to explain the luminosity, and he thinks it is due to the oxidation of a very volatile oxide of phosphorus. Lord Rayleigh showed that phosphorus may be slowly oxidized under conditions where there is no perceptible glow; the rate of oxidation was found to increase perceptibly with the vol. of the surrounding oxygen; and that the oxidation occurs in the gas as a reaction between oxygen and phosphorus. Phosphorus is slightly volatile at ordinary temp., and the increased volatilization which occurs when the press. of the gas is diminished appears to account for the increased luminescence in a rarefied atm. Hydrogen, carbon dioxide, and nitrogen containing a trace of oxygen become luminous in contact with phosphorus owing to the diffusion of the vapour of phosphorus in these gases. According to J. Chappius, ozone passed into oxygen in contact with phosphorus, at a temp. and press. at which no luminescence occurs, immediately produces a glow which continues so long as ozone is present. As J. Chappius showed, neither ozone nor the glowing is produced in oxygen at ordinary temp. and press., but on warming, both ozone and luminosity are produced. Hence, T. E. Thorpe said that when phosphorus is placed in oxygen, or in an atmosphere containing oxygen, under such conditions that it volatilizes, the phosphorus oxidizes, partly into phosphoric oxide and partly into phosphorous oxide (*q.v.*). Ozone is formed, possibly by the reaction already indicated, and this reacts upon the residual phosphorus vapour and the phosphorous oxide, with the production of the luminous effect to which the element owes its name. The glow itself is nothing but a slowly burning flame, having an extremely low temperature, caused by the chemical union of oxygen with the vapours of phosphorus and phosphorous oxide. By suitable means this glow can be gradually augmented until it passes by regular gradation into the active vigorous combustion which we ordinarily associate with flame. H. Biltz and A. Gross concluded that phosphorus trioxide is the primary product in the oxidation of phosphorus, and that the pentoxide is formed in a subsequent reaction. L. Marino and C. Porlezza said that three different stages are reached in the oxidation of phosphorus according to conditions employed: (i) formation of P_2O_5 when phosphorus vapour burns completely in excess of oxygen; (ii) formation of P_2O_3 and P_4O when phosphorus is burnt in a current of air; (iii) formation of a lower oxide, probably P_4O, when phosphorus is oxidized with highly diluted oxygen. According to J. Chariton and Z. Walta, when phosphorus is oxidized by oxygen at a press. in the vicinity of 10 mm., the reacting mol. is P_2; when this is oxidized, more mols. are formed from P_4 with absorption of heat; this, together with the fact that some of the heat of oxidation is lost as radiation, prevents the rapid action. The higher the press. of the phosphorus vap. the greater is the proportion of P_4 mols. and the higher is the critical press. of the oxygen. The argon diminishes the loss by radiation, receiving energy by collision, which is then communicated to the phosphorus by further collisions and the critical press. is reduced. The subject was discussed by M. Bodenstein.

The glow of phosphorous oxide presents similar features to the glow of phosphorus itself. Consequently, as just indicated, it has been inferred that the glow of phosphorus is due to the phosphorous oxide formed in a preliminary non-luminous oxidation. A. Petrikaln found that the ultra-violet bands in the spectrum of glowing phosphorus have maxima at 3270, 2600, 2530, 2460, and 2390 A., in agreement with the bands in the arc-spectrum of phosphorus pentoxide. The spectral observations of H. J. Emeléus and co-workers show that the light from burning phosphorus, that from glowing phosphorus, that from glowing phosphorous oxide, and that from spontaneously inflammable phosphine burning in oxygen give the same spectrum—*vide supra*, phosphorus. H. J. Emeléus added:

> The fact that the light from glowing phosphorus and that from phosphorus trioxide both give the same spectrum supports the analogy between these two oxidations, already well established in other respects. These observations, however, cannot be taken as proof of the identity of the chemical processes. They indicate rather that there is some radiating system involved in them all, which gives rise to a definite band spectrum. Such a system may well have a connection with the chemical anomalies common to the low temperature oxidation of these phosphorus compounds.

W. E. Downey showed that the action of the light, through windows of quartz or fluorite, on glowing phosphorus, formed ozone. Similarly, it was found that the formation of ozone by glowing phosphorus is proportional to the intensity of the glow, although a fresh phosphorus surface did not show this until it had become acclimatized. The glow of phosphorus trioxide was similar but of less intensity. A. L. Hughes showed that the spectrum of the glow extends within the region λ=1200–1800 A. The glow is capable of ionizing air. These facts, said W. E. Downey, support the idea that *the ozone is formed by the glow of phosphorus.* W. Busse could not repeat the experiment, and he doubted if rays between λ=120 A. and 200 A. are generated at all. W. Busse, and A. Petrikaln also showed that the production of ozone is not a photochemical effect of the glow.

C. F. Schönbein assumed that the ozone formed during the reaction is a necessary catalyst, and that it is destroyed by those agents which inhibit the glow. H. J. Emeléus showed that were this so, the relative effect of different retarders would be that of their reactivity towards ozone. In some cases this is not so—*e.g.* acetone is less readily attacked by ozone than is benzene, and yet it is a stronger inhibitor of the glow. M. Centnerszwer showed that it is not likely to be due to the formation of a protective film on the phosphorus because phosphorus exerts its normal vap. press. in the presence of inhibitors. It is generally supposed that the glow is a process analogous to the passage of flame through a combustible mixture, and that poisons prevent this occurring. Thus, Lord Rayleigh found this to be the case with the inhibition produced by an excess of oxygen; and L. and E. Bloch measured the blast of gas necessary to blow the glow from a given phosphorus surface in various oxygen-nitrogen mixtures, and found that it becomes less as the percentage of oxygen was increased. Assuming that the blast required to maintain the glow in a stationary position downstream is a measure of the virtual rate of propagation upstream, it follows that successive increases in the oxygen conc. decrease the rate of propagation. H. J. Emeléus studied the inhibitory effect of benzene, chloroform, aniline, and ethylene on the glow. A decrease of press. or an increase of temp. favours the glow, while the presence of air increases both the vap. press. and reactivity of the phosphorus. He found that the inhibition with ethylene can occur at 90°, which is much above the normal ignition temp. of phosphorus. Moreover, the "glow temperature" does not depend on whether air or oxygen is used as a diluent for ethylene. When the glow is prevented, the reaction continues; this is shown by the slow non-luminous oxidation which still occurs at 48°. At some stage, depending on the conc. of the ethylene, some kind of impediment is overcome, and a wave of luminosity passes through the mixture, the subsequent oxidation being accelerated by the formation of ozone. Again, on slowly decreasing the press. of a mixture of ethylene and oxygen, the partial press. of the phosphorus will remain constant in the presence of the solid. In effect, therefore, the proportion of combustible vapour in the mixture is being increased, which in itself would be expected to favour flame-propagation. Analogous cases of the retardation of combustion have been reported by A. G. White, H. B. Dixon, M. Delépine, etc. The experiments of H. J. Emeléus showed that the addition to air of typical inhibitors renders it easier to blow the glow from a phosphorus surface, and that increase in temp. diminishes this action. An analogy is thus established between the action of an excess of oxygen and that of the stronger inhibiting agents in that both prevent the propagation of the glow in the gas. A tentative explanation of the mechanism was put forward by Lord Rayleigh, who suggested that in the propagation of the glow products of the reaction in one layer acted as catalysts in the next. These catalytic particles are supposed to be rendered inactive by the adsorption of the mols. of the inhibiting gas, when the reaction stops. A similar view has been adopted by H. B. Dixon to explain the inhibition of the phosphorescent flame of carbon disulphide.

The formation of ozone, takes place in such a way that the amount of ozone formed is proportional to the amount of phosphorus oxidized, and also that the *atomic* ratio of the number of atoms of phosphorus oxidized to the number of molecules of ozone formed is 2 : 1. C. Matteucci showed that air in the vicinity of oxidizing phosphorus becomes charged electrically. Both positively and negatively charged electroscopes in the vicinity of oxidizing phosphorus are discharged showing that both negative and positive ions are produced in air: $O_2=O^-+O^+$. Thus, A. C. Christomanos found that a piece of paper moistened with an ethereal soln. of phosphorus will discharge a positively or a negatively charged electroscope. The subject was studied by J. A. McClelland and P. J. Nolan, etc. N. R. Dhar said that phosphorescence, like fluorescence, is due to molecules which have been activated by ions formed in the oxidation of the phosphorus, returning to the normal state.

The phenomenon is illustrated by the following experiment: A large test-tube *A*, Fig. 11, and a two-necked bottle, *B*, are fitted as indicated in the diagram; the two-necked bottle is connected with a metal cylinder, *C*, fitted with a brass rod attached to the charged electroscope *D*. The metal cylinder is fitted with a rubber stopper and a tube leading to an aspirator. The metal cylinder is put in electrical connection with the earth. The aspiration of air through the system has no appreciable effect on the gold-leaf of the electroscope; but if a little phosphorus be placed in the tube *A*, the electrical conductivity of the air is shown by the movement of the gold-leaf of the electroscope. The attachment *A* can be modified to find if the ambient air becomes electrically conducting during other chemical processes.

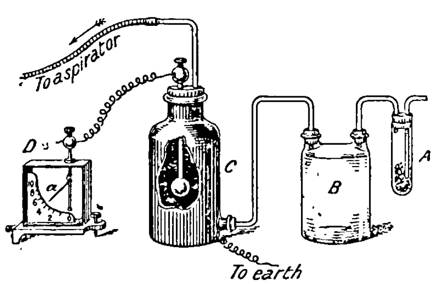

FIG. 11.—Experiment showing the Ionization of Air during the Oxidation of Phosphorus.

It is not clear what actually takes place during oxidation of phosphorus. A number of more or less plausible hypotheses have been proposed. B. C. Brodie, and C. F. Schönbein suggested that during the process of oxidation, the oxygen is split up into two parts which take up electrical charges of opposite sign. As R. Clausius expressed it, " phosphorus resolves the oxygen molecule into two atoms of opposite electrical states, one of which combines with the phosphorus and the other is removed from the sphere of the reaction." The subject was discussed by H. L. F. von Helmholtz, R. von Helmholtz and F. Richarz, J. J. Thomson, J. Elster and H. Geitel, W. Giese, A. Gockel, A. Schuster, E. Bloch, F. Harms, H. Löwy, etc. The general idea is that the conductivity of the ambient air when phosphorus is oxidizing is really due to the ionization of the oxygen molecules; G. C. Schmidt, however, thinks that the conductivity is due to " the convection of electricity by cloud-forming, conducting oxidation-products"; and F. Harms attributed the ionization to a secondary action due to the ozone; he said that, as indicated by F. Richarz and R. Schenck, no ionization occurs during the combustion of phosphorus. On the other hand, G. C. Schmidt said that burning phosphorus makes the air a good conductor, and that the conductivity rapidly decreases with the desiccation of the air. R. Schenck and E. Breuning attribute the ionization to a reaction product, a kind of *phosphorus emanation*, which undergoes complete condensation at —180°, but has an appreciable vapour pressure at —80°. W. Busse showed that phosphorus is luminous when it is undergoing slow oxidation with the concomitant formation of ozone and the appearance of positively and negatively charged ions in the surrounding gas. F. Harms, and E. Bloch studied the mobilities of the ions, and W Busse found that the ions are generated on the oxidizing phosphorus. The two kinds of ions do not at first show different mobilities. There is afterwards a continuous increase in the size of ions, and the presence of a continuous range of sizes can be demonstrated. Consequently, the phosphorus is not the only place at which ions originate; and the rate of growth of the large ions shows that ionization also occurs in the stream of air away from the phosphorus. The high mobilities of the negative ions is ascribed to multiple charges—four to six times as great as those carried by the positive ions. Most of the positive ions carry single charges, and in any case four charges is the maximum carried by a positive ion. On the assumption that the positive ions carry single charges, it can be shown that in the ageing process the positive ions change in size from 5×10^{-8} cm. to from 2×10^{-8} to 4×10^{-8} cm. in 8 seconds. W. Busse found that the ionization-temp. curves show maxima and minima and a noteworthy small peak at temp. between 35° and 40°, *i.e.*, just below the flashing temp. In dry air, ionization occurs only at higher temp. The position and magnitude of the maximum are greatly influenced by the temp. of the air stream. The moisture present favours a rapid rise to maximum ionization. The fact that moisture appears to be essential for the formation of ions, the fact that the negative ions take up multiple charges preferentially, lead to the view that the ionization occurs as a result of the dissociation of an acid formed in the course of the oxidation of phosphorus. The charge which occurs, initially, on passing a stream of air over the phosphorus is, apart from special exceptions, equal to the charge at the stage immediately preceding the ignition. On the other hand, the maximum in the curve corresponds with a charge several times as great as the initial charge. The amount of dissociating acid present remains fairly constant, so that ionization by stages must occur. It is concluded that pyrophosphoric acid must be the dissociating substance responsible for ion-formation.

R. Schenck and co-workers found the conductivity of ozone is not increased by contact with organic substances such as turpentine, amylene, eugenol, caoutchouc, silk, cotton-wool, linen, or wood, whilst that of air is not increased by contact with benzaldehyde, formaldehyde, acetaldehyde, methyl, ethyl, or amyl alcohol, methyl or ethyl ether, phenylhydroxylamine, indigo-white, pyrogallol, or triethylphosphine, or by the slow oxidation of sulphur or of bromoacetylene, which resembles phosphorus in that when slowly oxidized it shows the phenomenon of intermittent phosphorescence and forms a polymeride, tribromobenzene. If the conditions are such that the oxidation of phosphorus is hindered, the increase in the conductivity of air or oxygen is correspondingly slight. Thus, the conductivity of pure oxygen in contact with phosphorus under atm. press. is much less than that of air under the same conditions. The conductivity of air which has been passed through turpentine, alcohol, mesitylene, ammonia, ethylene, or amylene is not increased by bringing the air in contact with phosphorus, but, on the other hand, the conductivity is diminished only slightly if the process is reversed. Mixtures of oxygen with hydrogen or carbon dioxide give the same result as air. The conductivity of air or of ozonized oxygen, but not of pure oxygen, is increased by contact of the gases with red phosphorus. They added that the conductivity of air in contact with glowing phosphorus is connected with the presence of phosphorus trioxide, and may be caused by the interaction of the trioxide and moisture to form phosphorous acid. E. Meyer and E. Müller inquired whether the ionization of the air in contact with oxidizing phosphorus is due to the light emitted in the process or to the oxidation itself. In the presence of substances such as chlorine, ether, and turpentine, which inhibit the glowing of phosphorus, there is no oxidation and no ionization. If phosphorus is allowed to oxidize in thin-walled quartz vessels which are transparent to ultra-violet radiation, no ionization of the air can be detected. The spectrum shows that the radiation emitted by phosphorus undergoing oxidation is free from ultra-violet rays. The ozone produced in the oxidation cannot be the cause of the enormous conductivity imparted to the air; after removal of the ozone, the air retains its conducting power. According to H. Schmidt, when a current of purified hydrogen, carbon dioxide, or nitrous oxide is passed through an emulsion of phosphorus in water or through a solution in benzaldehyde, the luminosity and cloud formation, which are observed in the early stages, gradually diminish in intensity, and disappear when the oxygen has been completely removed. When the inactive gases charged with phosphorus vapour are passed into the chamber of an electroscope, ionization currents are obtained, which are very much larger than the currents obtained when air similarly saturated with phosphorus vapour is passed into the chamber. On passing pure oxygen through the emulsion or solution, the luminosity and cloud formation disappear as the partial pressure of the oxygen rises in consequence of the removal of air.

One form of the ionization hypothesis assumes that *atoms* of oxygen alone take part in the oxidation, and that some of the molecules of oxygen are dissociated into two atoms, each atom acquiring at the same time an electric charge of opposite sign: $O_2=O^++O^-$. The phosphorus combines with the atoms with one kind of electric charge; and the atoms of oxygen with a charge of opposite sign form ozone. The dissociation of the oxygen molecule is not a consequence of the oxidation, but antecedent to it, as suggested by O. Loew, and H. Fudakowsky. This view is confirmed by T. Ewan, who showed that when the partial press. of the phosphorus is less than 100 mm. the rate of oxidation of the phosphorus is proportional to the square root of the partial press., and not to the partial press. itself. J. H. van't Hoff interpreted this to mean that the actual oxidation of the phosphorus is effected by the atoms of the dissociated oxygen molecules; in symbols: $2P+2O_2=P_2O_3+O$, and $O_2+O=O_3$. According to W. Ostwald, this hypothesis cannot be right, because ozone has more available energy than oxygen from which it is derived, and energy must therefore be added to oxygen to produce ozone, the assumption being that the chemical energy of one reaction is not available for another totally different reaction, so that the energy degraded during the oxidation of phosphorus cannot be used for producing ozone. A. Bach assumed that a peroxide is first formed by the direct addition of oxygen to phosphorus, and this, on contact with water, forms an oxide of phosphorus and hydrogen dioxide. W. Ostwald likewise assumed that each atom of phosphorus is first oxidized by direct union with whole molecules of oxygen, forming a higher peroxide, say, P_2O_{2n}. This then decomposes, giving atomic oxygen: $P_2O_{2n}=P_2O_{2n-3}+O_3$. E. J. Bowen and E. G. Pells showed that if phosphoric acid is the final product of the oxidation of phosphorus, and is produced by a series of consecutive reactions of which only one, involving only one mol of oxygen, emits light, then, the ratio of the number of quanta of visible light emitted to the number of molecules reacting in the glow of phosphorus vapour and oxygen shows that at least one in 2000 molecules of phosphorus undergoing oxidation emits a quantum of visible light. The glow of phosphorus is a kind of chemiluminescence in which oxidation at the surface of solid particles of an oxide excites to luminescence the adsorbed molecules of some other oxide. This subject was discussed by H. Kautsky.

When phosphorus is oxidized in darkness in the presence of a solution of indigo, the luminosity, which is a sign that phosphorus is undergoing oxidation, gradually disappears; if the contents of the vessel be now shaken up, the luminosity reappears. Hence something which retards the further oxidation is formed, and this product is destroyed by shaking up with indigo soln. The alternate appearance and disappearance of the luminosity may be produced again and again. At the same time the blue colour of the indigo soln. gradually disappears, showing that the primary product of the oxidation of phosphorus is absorbed by the indigo soln. From this experiment, J. H. van't Hoff thinks that the primary product of the action cannot be ozone, because J. Chappius has shown that the presence of ozone would accelerate the oxidation. Something which retards the oxidation must be present. Merely shaking up the water, without the indigo, will not remove the primary product of the oxidation. He suggested that this product is an excess of positively or negatively charged oxygen atoms. Whatever may be the product which prevents oxidation, it gradually disappears when the flask is left alone, and the luminosity, in consequence, reappears in a few hours; again oxidation ceases, to begin anew on standing a few hours. This explains the *periodic phosphorescence* noticed by J. Joubert in 1874. The subject was studied by Lord Rayleigh, and W. P. Jorissen. K. R. K. Iyer found that the periodic phenomenon occurs in the presence of air when traces of inhibitors like naphthalene, carbon disulphide, turpentine, light petroleum, etc., are present, but not with water alone.

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§ 7. The Chemical Properties of Phosphorus

Yellow phosphorus is commonly sold in the form of waxy, transparent sticks which are usually preserved under water, because the element is so readily oxidized and inflamed when exposed to air. Yellow phosphorus fumes in air, and it then appears to have a peculiar odour recalling that of garlic. As remarked by C. F. Schönbein,[1] phosphorus vapour has probably no smell; what is actually perceived is the smell of a mixture of phosphorous oxide and ozone. T. E. Thorpe and A. E. H. Tutton also showed that the fumes of phosphorus consist largely of phosphorous oxide; by drawing air over phosphorus without allowing it to ignite, and passing the fumes through a narrow strongly-cooled tube, a deposit is obtained which melts with the warmth of the hand, and gives the reactions for phosphorous oxide. Moreover, the odour of the product is identical with that of pure phosphorous oxide, and it is also identical with the peculiar smell noticed in a lucifer-match manufactory during the making and handling of the "composition" with which the splints are tipped, and which is present in the neighbourhood of the benches where the "boxers" are at work. Red phosphorus is inert under many circumstances where yellow phosphorus is an active chemical agent; and it has a far smaller tendency to unite with incandescence with other substances. Yellow phosphorus is not very soluble in most of the common solvents; carbon disulphide is considered to be *the* solvent for this element; and, as indicated in detail below, the solubility in other solvents is much smaller—thus, 100 grms. of solvent dissolve approximately:

Carbon disulphide.	Benzene.	Almond oil.	Conc. acetic acid.	Ether.	Alcohol, sp. gr. 0·822.	Glycerol.
25	1·5	1·00	1·00	0·45	0·25	0·17 grm.

W. Ramsay and J. N. Collie [2] observed no reaction between **helium** and phosphorus, although R. J. Strutt observed that a little helium may be absorbed. Lord Rayleigh and W. Ramsay observed no reaction between phosphorus and **argon.** W. Ramsay and F. Soddy observed no reaction between phosphorus and radium emanation or **niton.** M. Guichard examined the gases occluded by phosphorus, and evolved when the element is heated in vacuo. H. Davy was very much impressed by the proportion of **hydrogen** liberated from phosphorus during the passage of an electric current; and H. B. Baker and H. B. Dixon showed that comparatively large quantities of hydrogen are absorbed or occluded by phosphorus. Hydrogen, however, as A. F. Fourcroy and L. N. de Vauquelin showed in 1822, exerts no appreciable chemical action if heated in contact with phosphorus. F. H. Newman observed that hydrogen is absorbed by phosphorus in the electric discharge tube. Although hydrogen *in statu nascendi* is able to unite with phosphorus, once the hydrogen has assumed the gaseous state, combination no longer occurs. I. Langmuir, however, observed that the so-called atomic hydrogen can convert phosphorus into phosphine. J. Davy said that hydrogen becomes charged with phosphorus vapour when in contact with that element. In 1894, J. W. Retgers stated that a stream of hydrogen passed over heated amorphous phosphorus does form hydrogen phosphides, but V. E. Tischtschenko and N. Zawoiko, and A. J. J. Vandevelde showed that there is no direct combination even when the phosphorus is heated to the temperature of sublimation. True enough, if hydrogen be passed over molten phosphorus, the vapour of phosphorus diffuses into the hydrogen imparting to it the odour of garlic, the property of emitting light when it comes in contact with oxygen, or the hydrogen may even ignite when it comes in contact with the air. The formation of a volatile hydrogen phosphide when phosphorus is in the presence of zinc and dil. acid, or conc. alkali generating hydrogen was observed by L. Dusart, and A. R. Leeds. According to J. B. A. Dumas, zinc in contact with dil. acids and phosphorus does not form hydrogen phosphide, and H. Davy was mistaken in supposing that combination occurred, for, if the acid is heated, phosphorus vapour not hydrogen phosphide may be carried along with the hydrogen; but J. Brössler, like H. Davy, considered that combination of phosphorus with the nascent hydrogen occurred under these conditions. V. Ipatieff and V. Nikolaieff observed that phosphine is formed when white phosphorus and hydrogen are heated in a sealed tube at 360°. Red phosphorus was found by V. Ipatieff to pass into the black variety when heated in hydrogen at 200° and 90 atm. press., whereas under milder conditions it furnishes phosphine, etc. V. Kohlschütter and A. Frumkin noticed that hydrogen and phosphorus vapour form solid hydrides when exposed to the luminous electrical discharge. They also found that phosphorus can adsorb argon and helium.

The effect of **oxygen** has been discussed in a special section, and the action of **ozone** is also there indicated. H. Biltz and A. Gross, J. Lang, and K. Brunner described a demonstration experiment for the combustion of phosphorus; N. R. Dhar observed that in the oxidation of phosphorus, by atm. oxygen, the presence of easily oxidizable substances like hydroquinone, sugars, glycerol, sodium arsenite, etc., retard its reaction. A. N. Dey and N. R. Dhar studied some coupled reactions with oxidizing phosphorus as the primary reaction and oxidizing sulphur, nickelous hydroxide, ethyl alcohol, sodium arsenite, or oxalic acid as the secondary reaction. The use of phosphorus for the production of smoke screens was discussed by H. W. Walker; and for the absorption of oxygen in gas analysis, by A. Holmes. N. R. Dhar, and C. Moureu and C. Dufraisse[3] discussed the spontaneous oxidation of phosphorus by free oxygen. A. Schrötter said that red phosphorus can be kept in air for years without change. J. Böeseken, G. Wilson, and J. Personne observed that moist red phosphorus in a finely divided state is slowly oxidized; and T. B. Groves observed that the smell of ozone is produced, but no luminosity occurs. A. Pedler also noted that in hot, moist, tropical atm., phosphine and phosphorous acid are formed. A. Stock and F. Gomolka added that moist red phosphorus, like yellow phosphorus, is oxidized by moist air, the only difference is that the oxidation is much slower. For the burning of phosphorus in air, *vide* the different oxides of phosphorus. L. Gmelin, and B. von Dybkowsky showed that phosphorus and **water** can react chemically at ordinary temp. A. R. Leeds believed that moist phosphorus, in an atm. of carbon dioxide, can form phosphine. A. Oppenheim found that water heated in a sealed tube with red or yellow phosphorus forms phosphine and phosphorous acid. J. J. Berzelius said that yellow phosphorus is very slightly soluble in **water**; and the solubility was also qualitatively observed by R. Phillips, J. Murray, and W. Müller-Erzbach. C. Stich said that 100 grms. of water can dissolve 0·0003 grm. of phosphorus, at 15°; J. Hartmann, 0·000127 grm. at 38·5°; and T. Bokorny said that an aq. soln. can be obtained containing 0·02 grm. of phosphorus in 100 c.c. of water by pouring a soln. of 0·1 grm. of phosphorus in carbon disulphide mixed with ether and hot alcohol, into 500 c.c. of air-free boiling water, and continuing the boiling until the alcohol, ether, and carbon disulphide have been expelled. C. F. Cross and A. Higgin found that only in the presence of air is the water decomposed; in an atm. of carbon dioxide, water can be distilled from phosphorus without forming phosphine, but under ordinary conditions, said T. Weyl, phosphorus decomposes warm water with the evolution of phosphine. C. Stich observed no activation of the oxygen when a soln. of 3 mgrms. of phosphorus in water is kept in intimate contact with air. C. F. Cross and A. Higgin, and J. Böeseken observed that red phosphorus does not react with boiling water, but at a higher temp. a feeble reaction occurs. V. Ipatieff and V. Nikolaieff observed that white phosphorus and water in a sealed tube at 360° yield phosphoric acid and phosphine; and the formation of phosphine starts at about 290° and 40–50 atm. press., and is indicated by a break in the temp.-press. curve. V. Ipatieff observed a little black phosphorus may be formed; and red phosphorus furnishes phosphoric acid and phosphine when heated under press. with water. H. Rebenstorff described a demonstration experiment for the ignition of phosphorus under water. T. Weyl found that a 6 to 30 per cent. soln. of **hydrogen dioxide** attacks phosphorus at about 60°, forming phosphine which does not spontaneously inflame, and phosphorous and phosphoric acids. The action of hydrogen dioxide on red or scarlet phosphorus is much more energetic than is its action on yellow phosphorus, the action being violent with soln. which contain more than 8 per cent. of the dioxide; the products are in this case also hydrogen phosphide, phosphorous acid, and phosphoric acid. Hydrogen phosphide is evolved when red phosphorus is boiled with water; the action is not due to any alkali derived from the glass vessels used. The liberation of phosphine by the action of red or scarlet phosphorus on boiling water or hydrogen dioxide is not due to the presence of yellow phosphorus, but rather to the formation and decomposition of phosphorous acid: $3H_2O_2+2P=2P(OH)_3$; and $4P(OH)_3=PH_3+3H_3PO_4$.

H. Moissan[4] showed that **fluorine** reacts on both red and yellow phosphorus at ordinary temp. The reaction is accompanied by incandescence producing the trifluoride if the phosphorus is in excess, and the pentafluoride if the fluorine is in excess. Ordinary phosphorus burns in **chlorine** gas with a pale greenish light producing, in an analogous manner, phosphorus tri- or penta-chloride. A. Schrötter said that no reaction with liquid chlorine occurs at the temp. of solid carbon dioxide, but, according to J. B. A. Dumas, and F. Donny and J. Mareska, it does react, even at —90°. Red phosphorus was found by A. Schrötter to react with chlorine at ordinary temp., forming first the tri- and then the penta-chloride; red phosphorus inflames in warm chlorine but the flame dies out if the gas be cooled. J. Personne observed that very finely divided red phosphorus inflames spontaneously in chlorine gas at ordinary temp., forming the pentachloride. A. Schrötter found that red phosphorus dissolves in chlorine-water more quickly than does ordinary phosphorus because there are more points of contact. W. Müller-Erzbach said that the affinity of chlorine must be greater than that of bromine for phosphorus because of the increased density of the products. Ordinary phosphorus was found by A. J. Balard, and C. Löwig to react with **bromine** gas with incandescence, forming the tri- or the penta-bromide. H. Rose, and V. Merz and W. Weith observed that when small pieces of yellow phosphorus are thrown into liquid bromine, the phosphorus takes fire and produces dangerous explosions. A. Schrötter found that red phosphorus also unites with bromine, at ordinary temp., with incandescence. Ordinary phosphorus unites with **iodine** at ordinary temp, and, according to C. L. Gazzaniga, at —24°, with the development of heat. The product inflames on contact with air. The reaction was studied by J. L. Gay Lussac, T. S. Traill, R. Boulouch, and K. I. Lissenko. According to A. Schrötter, the reaction does not occur at ordinary temp. with red phosphorus, but when warmed, di- and tri-iodides are formed without incandescence. F. Sestini studied what he called the *chemical adherence* of red phosphorus to the metalloids. He found that the reddish-violet soln. of iodine in carbon disulphide is decolorized by dry red phosphorus. R. N. Traxler and F. E. E. Germann observed that after decolorization, the phosphorus contains hydriodic and phosphorous acids, but no free iodine. N. E. Gordon and J. C. Krantz used benzene, toluene, xylene, carbon disulphide, carbon tetrachloride, and chloroform as solvents for the iodine. G. Gore said that yellow phosphorus is not affected by liquid **hydrogen chloride.** A. Oppenheim found that hot conc. **hydrochloric acid** reacts with red phosphorus in a sealed tube at 200°, forming phosphine, etc.; $2P+3HCl=PH_3+PCl_3$. H. Rose said that several **metal chlorides** give off chlorine when treated with yellow phosphorus. O. Damoiseau found that yellow phosphorus does not react with **hydrobromic acid;** but in a sealed tube at 100°–120°, phosphonium bromide is formed. He also found that **hydrogen iodide** reacts with ordinary phosphorus at room temp., forming both the tetraiodide, and phosphonium iodide. With red phosphorus there is no reaction at temp. below 100°—the little phosphonium iodide which may be produced probably comes from the presence of yellow phosphorus as impurity. A. Oppenheim found that when red phosphorus is heated with **hydriodic acid** in a sealed tube at 160°, crystals of phosphonium iodide are formed. A. J. Balard showed that **hypochlorites** oxidize yellow phosphorus to phosphoric acid. N. A. E. Millon found that ordinary phosphorus reacts explosively with **chlorine trioxide;** and F. Stadion, and H. Davy observed a similar result with **chlorine dioxide.** J. Schiel found that an aq. soln. of **chlorous acid** immediately dissolves red phosphorus. R. Böttger found that if a drop of a soln. of phosphorus in carbon disulphide be placed on some powdered **potassium chlorate,** an explosion occurs as the solvent evaporates. J. W. Slater said that phosphorous and phosphoric acids are formed when phosphorus is boiled with a soln. of potassium chlorate. A. Schrötter found that when red phosphorus is triturated with potassium chlorate there is a vigorous reaction, and under water in the presence of sulphuric acid, there is a vigorous reaction without incandescent phenomena. M. Bengieser, and A. Ditte found that yellow phosphorus reacts with **iodic acid,** forming phosphorus oxides, iodine, phosphoric acid, and possibly red phosphorus; and M. Bengieser showed that **periodic acid** oxidizes phosphorus to phosphoric acid. According to T. F. Buehrer and O. E. Schupp, when either white or red phosphorus is mixed with potassium iodate, and a few drops of water are added, the mixture reacts violently, sometimes even explosively, liberating iodine and evolving a considerable quantity of heat. When more water is initially taken, the rate of the reaction is greatly decreased. Since the reaction starts slowly and gradually speeds up, it appears probable that the iodine formed is responsible for the rapidity of the reaction rather than the iodate ion. Since phosphorous acid is formed to a considerable extent under these conditions, the rate of the entire reaction is determined solely, perhaps, by the rate at which it is oxidized to phosphoric acid. It is possible, however, under suitable conditions, to render this oxidation complete by means of potassium iodate. The reactions involved in the oxidation of phosphorus by potassium iodate have been found to take place as follows: $5P+3IO'_3+3H^{\cdot}+6H_2O=\frac{3}{2}I_2+5H_3PO_3$. This reaction is slow, and goes partially to phosphoric acid. $2P+3I_2+6H_2O=6H^{\cdot}+6I'+2H_3PO_3$. This reaction is quite rapid. $5H_3PO_3+2IO_3'=I_2+3H^{\cdot}+5H_2PO'_4+H_2O$. This reaction is very slow, as is strikingly shown by adding potassium iodate to a phosphorous acid soln. Very little iodine is liberated even on refluxing the soln. for some time. $H_3PO_3+I_2+H_2O=3H^{\cdot}+2I'+H_2PO'_4$. This reaction has been studied by B. D. Steel, who finds that "two distinct reactions occur . . . one of which preponderates in acid soln. and the other in the absence of strong acid," the one in acid soln. being catalyzed by hydrogen ion. This reaction has been shown by others to be slow, and to depend in large measure upon the conc. of the acid. It is probable that the oxidation of the phosphorous acid by iodine determines the rate of the reaction as a whole: $5I'+IO'_3+6H^{\cdot}=3I_2+3H_2O$. This reaction is known to be instantaneous and complete.

According to B. Pelletier,[5] F. Isambert, A. Levol, and R. Böttger, when a mixture of **sulphur** and yellow phosphorus is warmed the two elements unite in all proportions with vivid combustion, and powerful detonations. The reaction is quite complicated, and a series of sulphides is formed—*vide infra.* W. Wicke said that the two elements unite at ordinary temp. when sulphur is in contact with yellow phosphorus under water. A. Schrötter observed no reaction with a mixture of sulphur and red phosphorus until the temp. attained 230°; nor did W. Spring obtain any evidence of combination when the mixture was subjected to great press. J. Davy found that when in contact with phosphorus, **hydrogen sulphide** becomes charged with the vapour of that element. F. Sestini found yellow phosphorus to be soluble in liquid **sulphur dioxide** without chemical action. F. C. Vogel observed that yellow phosphorus inflames at ordinary temp. after it has stood some time in the vapour of **sulphur trioxide,** and sulphur is produced. R. H. Adie obtained a complex $3P_2O_4.2SO_3$ by the interaction of yellow phosphorus and sulphur trioxide. He said that when a piece of phosphorus is dropped into liquid sulphur trioxide, it reduces the latter with violence to sulphur dioxide, and is itself oxidized, forming a white, flocculent solid, $3P_2O_4.2SO_3$, floating in the liquid. When the pieces of phosphorus were large, the heat of combination raised the temp. of the phosphorus sufficiently high to ignite it. Heating phosphorus with sulphur trioxide in a sealed tube not only oxidizes all the phosphorus, but converts it at once into phosphoric anhydride, which forms a clear soln. in the trioxide. A. Oppenheim showed that yellow phosphorus inflames when placed in a capacious flask containing conc. **sulphuric acid** heated to its b.p.; and when yellow phosphorus and the conc. acid are heated in a sealed tube at 200°, sulphur dioxide is formed : $3H_2SO_4+2P=2H_3PO_3+3SO_2$. A. Schrötter, and J. Pelouze observed no reaction between cold conc. sulphuric acid and red phosphorus, but when heated nearly to the b.p., sulphur dioxide is evolved. K. Heumann and P. Köchlin showed that **chlorosulphonic acid** reacts feebly with yellow phosphorus at ordinary temp., but a vigorous reaction begins at 25°–30° with the evolution of sulphur dioxide and hydrogen chloride, and ending with an explosion; with red phosphorus, a higher temp. is needed to start the reaction—it is assumed that phosphoric acid and a phosphorus chloride are first formed, and that these react with the sulphuric acid which is formed at the same time so as to produce phosphoryl chloride. They also found that **sulphuryl chloride** when warmed with yellow phosphorus reacts only feebly, while with red phosphorus the reaction is vigorous: $3SO_2Cl_2+2P=2PCl_3+3SO_2$; and that **pyrosulphuryl chloride** reacts vigorously with red phosphorus, forming phosphorus trichloride, etc. H. F. G. de Claubry found that ordinary phosphorus reacts with **sulphur monochloride,** S_2Cl_2, at 40°, with the development of heat, and the formation of sulphur and phosphorus trichloride. F. Wöhler found that yellow phosphorus readily dissolves in sulphur monochloride, and there is a reaction which M. Chevrier symbolized : $3S_2Cl_2+2P=2PSCl_3+4S$. P. Nicolardot found that yellow and red phosphorus dissolves in sulphur monochloride. J. J. Berzelius[6] found that **selenium** and yellow phosphorus are miscible in all proportions at a temp. near the m.p. of phosphorus ; the reaction is probably a complicated one as in the case of phosphorus and sulphur. E. Baudrimont found that when phosphorus reacts with **selenium monochloride,** Se_2Cl_2, phosphorus trichloride and selenium are formed ; and a similar result is obtained with **selenium tetrachloride,** but if this agent is present in excess, the complex $2PCl_5.SeCl_4$ is formed. L. Rosenstein found that soln. of **selenates** are reduced to the element or a phosphide when boiled a few minutes with red phosphorus; while **tellurates** are but slowly reduced.

Phosphorus does not react directly with **nitrogen.** F. H. Newman[7] found nitrogen is absorbed by phosphorus in the electric discharge tube. J. Davy noticed that in contact with phosphorus, nitrogen becomes charged with the vapour of that element. C. L. Berthollet attributed the faint luminosity of nitrogen charged with phosphorus vapour to the presence of oxygen as an impurity ; he also thought that when the gas is charged with phosphorus vapour it increases by 0·025 part of its vol., but C. Brunner could not verify this—only a milligram of phosphorus is taken up by 1732 c.c. of gas. By passing an electric discharge through a mixture of phosphorus vapour and nitrogen, V. Kohlschütter and A. Frumkin obtained solid nitrides—*vide infra*, phosphorus nitride. F. W. Bergstrom found that both yellow and red phosphorus react readily with **potassium amide,** and with **sodium amide,** W. P. Winter said that sodium phosphide as well as oxyacids of phosphorus, and a phosphorus amide are formed. According to H. Davy, **nitrous oxide** has no action on phosphorus even when that element is touched with a piece of red-hot iron ; but if the iron be still hotter, the phosphorus may inflame, forming phosphorus pentoxide, free nitrogen, and some nitrogen peroxide ; J. Dalton found that feebly burning phosphorus is extinguished in **nitric oxide ;** but at a higher temp., say at the m.p. of phosphorus, there is a vigorous reaction with the formation of nitrogen peroxide, etc. ; P. L. Dulong found that phosphorus ignites when strongly heated in **nitrogen peroxide** and burns vigorously. These results were confirmed by A. Rosenheim and J. Pinsker. R. Weber found that phosphorus also burns vigorously in contact with warm **nitrogen pentoxide.** H. Reinsch showed that phosphorus is but slightly attacked by **nitric acid** in an open vessel, at ordinary temp., because it becomes covered with a film of oxide; if air be excluded, nitric oxide is evolved, and the liquid becomes blue. The boiling acid, out of contact with air, forms nitric oxide, which reacts with the phosphorus, forming nitrogen ; if air be not excluded, the nitric oxide is not decomposed in this way. C. F. Schönbein showed that the heat may be such that phosphorus vapour rises and burns in the vapour of the nitric acid. According to C. Wittstock, hot nitric acid of sp. gr. 1·2 dissolves yellow phosphorus with the evolution of nitric oxide and nitrogen, and the formation of phosphorous and phosphoric acids; when the liquid is evaporated, the phosphorous acid is oxidized, and phosphoric acid is alone obtained. The reaction was studied by C. W. G. Kastner, L. A. Buchner, J. Geiseler, J. von Liebig, C. F. Bärwald, etc. There is some doubt about the nature of the gases evolved. J. Personne, and E. J. Maumené found that ammonia is a product of the reaction; and C. Montemartini showed that on exposing red phosphorus to the action of an excess of 17·3, 28·3, and 68 per cent. nitric acid, at 13°–14°, until all is dissolved, one gram of phosphorus furnishes respectively 0·0739, 0·0824, and 0·0095 grm. of ammonia. The phosphorus requires some days to dissolve in dil. nitric acid, but dissolution is rapid in the conc. acid. A. Schrötter found that red phosphorus is more easily attacked by nitric acid than yellow phosphorus; and J. Böeseken found that with boiling nitric acid of sp. gr. 1·25, half the phosphorus is oxidized to phosphoric acid, and half to hypophosphoric acid. A. Siemens showed that when a soln. of yellow phosphorus in benzene is treated with dil. nitric acid, and warmed to drive off the benzene, phosphorus pentoxide is present in the remaining liquid; with red phosphorus, some picric acid is produced. E. Marchand showed that yellow phosphorus burns in molten **ammonium nitrate,** forming phosphorus pentoxide. J. W. Slater found that a mixture of a **nitrate** with yellow phosphorus detonates by percussion; and a soln. of **barium nitrate** is not affected when boiled with phosphorus. A. Schrötter observed red phosphorus does not detonate when triturated with potassium nitrate, but when warmed together there is a vigorous reaction.

According to C. W. Böckmann,[8] and A. Vogel, ordinary phosphorus forms a dark brown powder in **ammonia** gas, but the earlier observations were made on imperfectly purified phosphorus. T. A. Commaille reported that ammonia gas has no action on phosphorus, though A. F. de Fourcroy found that a mixture of ammonia and phosphorus vapour decomposes into nitrogen and phosphine when led through a red-hot tube. C. Hugot was able to distil phosphorus unchanged in an atm. of ammonia. Aq. ammonia exerts a slight action on yellow phosphorus, particularly if heated, phosphine and a black powder are formed; but, according to F. A. Flückiger, red phosphorus is not soluble in that menstruum. G. Gore, and E. C. Franklin found that yellow phosphorus dissolves slowly in liquid ammonia; while E. C. Franklin, and C. Hugot said that red phosphorus is insoluble in this menstruum. According to A. Stock and co-workers, liquid ammonia blackens scarlet phosphorus. A. Stock and co-workers, R. Schenck, and C. Hugot showed that ordinary phosphorus reacts very slowly with liquid ammonia in a sealed tube at ordinary temp.—the soln. first becomes red, and in a few days it deposits a black powder. The reaction is much more rapid if the temp. be raised. The black product is supposed to be a compound of phosphorus hydride, P_4H_2, with ammonia —either $HP_4.NH_4$, or $P_4H_2.NH_3$—and a similar compound obtained by R. Schenck is formed by warming a mixture of ammonia with the solid hydride. R. Schenck represented the reaction: $14P+7NH_3=3P_4H(NH_4)+2(HN:P.NH_2)$. When the solid hydride is treated with piperidine, $C_5H_{11}N$, an analogous product, $P_4H_2(C_5H_{11}N)$, is formed—*vide supra,* phosphorus amides and imides; and *vide infra,* hydrogen triphosphide. According to C. Hugot, **sodammonium,** $Na.NH_3$, reacts with red phosphorus, forming ammonium and sodamide together with a substance with the ultimate composition, $Na_3P_2H_3$, in yellow needle-like crystals; $6NH_3Na+2P=P_2H_3Na_3+3NaNH_2+3NH_3$. W. P. Winter found phosphorus acts energetically on **sodamide,** forming a chocolate-brown powder which when heated gives off ammonia and phosphine, forming sodium phosphite and hypophosphite. C. A. Lobry de Bruyn found that phosphorus reacts with **hydrazine,** forming a black substance; and it dissolves slowly in **hydrazine hydrate,** forming a soln. which is coloured yellow, red, brownish-violet, and finally black; a little phosphine is given off, and water precipitates brown flecks. According to J. W. Dito, yellow phosphorus slowly dissolves in hydrazine hydrate, and if the mixture be left in vacuo for a couple of months, a black substance mixed with white crystals is formed. The white crystals are either hydrazine phosphite or hypophosphite; and they can be extracted by solution in alcohol in which the black mass is insoluble. When the black mass is exposed to the air it becomes yellow, and when heated in hydrogen to 100° it forms a red product similar to that which is formed by the action of phosphorus on free hydrazine. The black mass is supposed to be a weak phosphorus acid free from nitrogen, and the red substance its hydrazine derivative.

H. Moissan[9] observed that yellow phosphorus heated in contact with **phosphorus trifluoride** *ne produit aucune réaction;* C. Poulenc found that with **phosphorus trifluodichloride,** at 120°, phosphorus trifluoride and trichloride are formed. P. Walden, and J. Böeseken found that yellow phosphorus is soluble in **phosphorus trichloride,** and J. H. Gladstone, that it reduces **phosphorus pentachloride** to the trichloride. B. Reinitzer and H. Goldschmidt reported the formation of a suboxide when yellow phosphorus is heated with **phosphoryl chloride** at 200°. G. S. Sérullas showed that yellow phosphorus dissolves in **thiophosphoryl** chloride; and J. H. Gladstone, in **thiopyrophosphoryl chloride.** C. Löwig found that yellow phosphorus dissolves in **phosphorus tribromide,** and E. Buck showed that the solubility of red phosphorus in that menstruum is diminished by long heating. He gave

	172°	185°	198°	218°
Initial conc. . . .	0·555	0·476	0·592	0·476
Final conc. . . .	0·374	0·397	0·416	0·592
Duration of heating .	34	24	18	17 hrs.

He found that with ordinary commercial red phosphorus with 98 per cent. phosphorus, there dissolved 0·056 and 0·108 per cent. of phosphorus in respectively 10 and 42 hrs., and with a finely-divided sample 0·092 and 0·116 per cent. phosphorus in 10 and 20 hrs. respectively. R. Schenck found that 100 grms. of phosphorus tribromide dissolved 0·2601 grm. of scarlet phosphorus at 172°, and 0·3634 grm. at 184°. E. Baudrimont showed that yellow phosphorus does not attack **phosphoryl bromide** at the b.p. L. Rosenstein found that soln. of **arsenates,** and **arsenic, antimony, or bismuth salts** are not reduced by boiling with red phosphorus; but W. Finkelstein found that a nitrobenzene soln. of arsenic trichloride is reduced by yellow phosphorus and arsenic is deposited. O. Ruff observed that phosphorus reacts with **antimony trichloride** in the presence of a little aluminium chloride. F. E. Brown and J. E. Snyder observed that **vanadium oxytrichloride** is without action on red or white phosphorus.

Moist yellow phosphorus in an atm. of **carbon dioxide** was found by A. R. Leeds[10] to produce some phosphine, but not to react with the carbon dioxide; and G. Gore showed that a sat. soln. of phosphorus in carbon disulphide has no action on carbon dioxide. J. Davy found that when in contact with yellow phosphorus, **carbon monoxide** and dioxide become charged with the vapour of that element; but A. F. de Fourcroy and L. N. Vauquelin thought that this was not the case with carbon dioxide. G. Gore showed that a mixture of **ammonium carbonate** and red phosphorus in a red-hot crucible forms phosphorus pentoxide. J. Davy found that phosphorus does not react with **carbonyl chloride** even at the sublimation temp. of that element.

J. W. Retgers said that yellow phosphorus is very soluble in **methylene iodide,** and red phosphorus insoluble. A. Vogel found that 100 parts of **carbon disulphide** dissolve 5·55 to 5·88 parts of yellow phosphorus; J. B. Trommsdorff said 12·5 parts; and R. Böttger, 5·0 parts. H. Giran also made some observations which E. Cohen and K. Inouye consider to be inaccurate; they found the solubility, expressed in grams of phosphorus per 100 grms. of soln., to be:

	−10°	−7·5°	−5°	−2·5°	0°	5°	10°
Solubility . .	31·40	35·85	41·95	75·00	81·27	86·30	89·80

The soln. sat. at —3·5° separates at —8° into two immiscible liquids. Some properties of soln. of yellow phosphorus in carbon disulphide were described by W. A. Lampadius, D. Brewster, R. Böttger, J. J. Berzelius, J. Murray, J. M. Eder, F. Scriba, E. Brunn, G. Gore, and O. Ohmann. M. Thiele found that when a soln. of yellow phosphorus in carbon disulphide is mixed with alcohol, the soln. remains clear, and in a few days deposits an orange-yellow, crystalline mass; ether forms a turbid liquid and deposits a lemon-yellow precipitate, probably yellow phosphorus. Chloroform, benzene, and ligroïn produce no perceptible change. Red phosphorus was found by A. Schrötter to be insoluble in carbon disulphide—*vide infra.* R. Boyle mentioned that yellow phosphorus dissolves in spirits of wine. According to J. A. Buchner, 100 parts of cold **ethyl alcohol** of sp. gr. 0·799 dissolve 0·312 part of phosphorus, and when warm, 0·417 part; G. F. Schacht gave 0·208 grm. per 100 grms. of absolute alcohol. The soln. has an acid reaction and contains some oxide. The chemical reaction which occurs when a mixture of phosphorus and alcohol is heated in a sealed tube at 250° was investigated by J. Berthaud, and when the mixture is exposed to light, by A. Pedler. J. B. Senderens studied red phosphorus as a catalytic agent in the dehydration of alcohols. A. Schrötter found red phosphorus to be insoluble in alcohol. A. M. Ossendowsky said that 100 grms. of **glycerol** of sp. gr. 1·256, at 15°–16°, dissolve 0·25 grm. of phosphorus. According to C. F. Bucholz, at 20°, 100 grms. of absolute **ether** dissolve 5 grms. of yellow phosphorus and ordinary ether, 0·417 grm.; while L. V. Brugnatelli found at 15·5°, respectively 1·25 and 0·417 grm. A. C. Christomanos found for the solubility of phosphorus in grams per 100 grms. of ether:

	0°	5°	10°	15°	20°	25°	30°	35°
Solubility . .	0·4335	0·62	0·85	0·90	1·04	1·39	1·75	1·9984

The sp. gr. of the soln. sat. at 15°, 20°, and 25° are respectively 0·7257 at 13°, 0·7187 at 19°, and 0·7283 at 19°. A. Schrötter found red phosphorus to be insoluble in ether. In light, the soln. soon becomes turbid, and decomposes. T. Svedberg said that both red and yellow phosphorus are perceptibly soluble in **isobutyl alcohol.** According to A. C. Vournasos, the vapour of yellow phosphorus at 200° acts on **sodium formate** in the presence of hydrogen, producing sodium oxalate, $(COONa)_2$, and phosphine: $2P+6HCOONa=3(COONa)_2+2PH_3$. G. Vulpius found that **acetic acid** dissolves about one per cent. of yellow phosphorus; C. Stich, 100 grms. of 90 per cent. acetic acid dissolves 0·105 grm.; and J. P. Boudet reported that vinegar dissolves phosphorus. G. Vulpius found that phosphorus is freely soluble in **stearic acid**; and C. Stich showed that at 15°, **oleic acid** dissolves 1·06 grm. of phosphorus per 100 grms. of acid. C. B. Mansfield said that yellow phosphorus is slightly soluble in cold and more soluble in hot **benzene**; and A. C. Christomanos, expressing the solubility in grams of phosphorus per 100 grms. of benzene, found:

	0°	5°	10°	20°	30°	40°	50°	60°	70°	81°
Solubility .	1·513	1·99	2·4	3·21	4·601	5·75	6·8	7·9	8·898	10·027

The soln. becomes turbid when exposed to air. A. Siemens said that the vaporization of a soln. of red phosphorus in benzene is quite different from that of a soln. of yellow phosphorus in that solvent. N. T. de Saussure found phosphorus to be soluble in 14 parts of hot **petroleum,** and less in cold; L. Crismer said it is slightly soluble in liquid **paraffin,** and C. Stich found 100 grms. of paraffin at 15° dissolve 1·45 grms. of yellow phosphorus. A. Colson said that ordinary phosphorus dissolves in **turpentine** only in the absence of air; and warm, rectified turpentine freely dissolves the phosphorus, which furnishes snow-white crystals on cooling; in the presence of air, the liquid becomes cloudy, and a white, odorous, colloidal mass is obtained: $(C_{10}H_{16}O_3)_2.H_3PO_4$; red phosphorus does not dissolve in turpentine even at 270°; with boiling turpentine, and other high boiling liquids, the red phosphorus may be partly converted into the yellow form, and it may then pass into soln. A. Schrötter stated that red phosphorus is slightly soluble in turpentine, but A. Colson said that this is not the case. There is no common solvent for yellow and red phosphorus; and since both varieties have the same vap. press., they would become identical in a common solvent. F. Molnar, A. Colson, and S. Minovici studied the chemical reaction between turpentine and phosphorus. As mentioned by R. Boyle, yellow phosphorus dissolves in a number of **essential oils,** and **fatty oils,** particularly when warm—*e.g.* oil of copaiba, oil of mandarin, oil of caraway, oil of aniseed, oil of cloves, oil of mace, etc. C. Stich said that at 15°, 100 grms. of oil of almonds dissolve 1·25 grms. of phosphorus. L. E. Jonas studied the chemical action of phosphorus on heated linseed oil, poppy oil, oil of almonds, and nut oil. F. Krafft and R. Neumann found that the arsenic in **triphenylarsine** is quantitatively displaced by phosphorus in a sealed tube at 300°; likewise also **triphenylstibine.** J. H. Hildebrand and T. F. Buehrer observed that the critical soln. temp. of liquid phosphorus with **decane** is over 300°; with **chlorobenzene,** 264°; **naphthalene,** 202°; **phenanthrene,** 200°; *p*-**dibromobenzene,** 163°; and with **carbon disulphide,** —6·5°. H. Wichelhaus investigated the chemical action of yellow phosphorus on **phenol, naphthol,** etc.; P. Bartolotti, on *rottlerin*—from the dyestuff kamala; and T. Weyl, the action of red phosphorus on **nitrobenzene.**

The slight solubility of yellow phosphorus in several other liquids has been noticed—*e.g.* ethyl chloride, ethylene chloride, chloroform, bromoform, chloral, acetic ether, acetone aldehyde, cacodyl sulphide, allyl thiocyanate, mercury methide, valerianic acid, amyl valerate, fusel oil, benzoyl chloride, stannic chloride, ethyl nitrite, nicotine, coniine, cavutchin, styrene, aniline, quinoline, creosote, etc. J. Hartmann found that 100 grms. of *bile* at 38·5° dissolved 0·02424 grm. of phosphorus, and more at a higher temp.

A. Kemp observed that yellow phosphorus slowly dissolves in liquid **cyanogen** and possibly forms cyanogen phosphide; but H. Hübner and G. Wehrhane observed no formation of that phosphide when cyanogen gas or **cyanogen chloride** is brought in contact with phosphorus vapour; C. Löwig observed a phosphorus bromide is formed by the action of **cyanogen bromide** on warm phosphorus; and F. Wöhler noticed that a phosphorus iodide is formed with incandescence when **cyanogen iodide** is brought in contact with molten phosphorus.

The action of phosphorus on the **metals** is discussed in connection with the phosphides—*vide infra.* According to A. Michaelis and M. Pitsch,[11] when ordinary phosphorus is warmed with an alcoholic soln. of **potassium hydroxide,** phosphine, hydrogen, and hypophosphorous acid are produced. It is maintained that the reaction proceeds in two stages: The phosphorus first dissolves, forming a dark red soln., and evolving a little gas which smells of phosphine; the filtered liquid gives a greenish-yellow precipitate when treated with hydrochloric acid, and this, when dried, consists of phosphorus tetritoxide: $4P+H_2O=P_4O+H_2$, and the nascent hydrogen converts a little phosphorus into phosphine. As the red soln. becomes warm, the tetritoxide passes into the hemioxide, $P_4O+H_2O=2P_2O+H_2$, and the hemioxide reacts with water, forming hypophosphorous acid: $P_2O+3H_2O=2H_3PO_2$—*vide infra,* phosphorus tetritoxide. By boiling an aq. soln. of alkali hydroxide with ordinary phosphorus, spontaneously inflammable phosphine is formed—*vide infra.* According to W. P. Winter, it is probable that sodium phosphide is one of the primary products of the action of phosphorus on sodium hydroxide, and this may, on hydrolysis, be the source of the phosphine. A. Schrötter found that when red phosphorus is boiled with potash-lye, the colour changes to a dark chocolate-brown, and phosphine, not spontaneously inflammable, is evolved. C. H. Burgess and D. L. Chapman said that finely-divided red phosphorus dissolves in an alcoholic soln. of alkali hydroxide; but A. Michaelis and K. von Arend, that red phosphorus is partly transformed into yellow phosphorus by grinding to a fine state of subdivision, and it then becomes soluble in the alcoholic potash-lye. Red phosphorus, whether commercial or prepared by heating phosphorous acid and phosphorus trichloride, is insoluble in aq. alcoholic potash; and when triturated with water for a long time, it is oxidized to the suboxide and acids of phosphorus. I. Guareschi found that **soda-lime** absorbs phosphorus vapour. W. Wicke said that a stick of phosphorus in contact with moist **copper oxide** partially reduces the oxide, forming in a few weeks crystals of copper. A. Schrötter said that copper oxide does not react when triturated with red phosphorus, but when heated together there is a vigorous reaction. There is, however, a vigorous reaction with **silver oxide** when the mixture is triturated or heated. A. Oppenheim found that **zinc oxide** is not attacked when heated with yellow phosphorus in a sealed tube; but B. Renault said that the vapour of phosphorus acts on zinc oxide at a red-heat, forming zinc phosphides, and similarly also with **cadmium oxide.** A. Schrötter found that when red phosphorus is triturated with **mercury oxide,** or one of the **lead oxides,** there is a vigorous reaction and likewise also when the mixture is warmed; **manganese dioxide** does not react by trituration, but it does so when warmed with red phosphorus. A. Thiel and H. Kölsch found phosphorus vapour reacts with **indium trioxide,** In_2O_3.

F. Wöhler found that when phosphorus was placed in a soln. of **copper sulphate,** phosphorus was deposited on the copper wire in contact with phosphorus, and W. Wicke obtained analogous results with **silver nitrate.** A. Vogel, and R. Böttger observed that ordinary phosphorus reduces copper from soln. of the **copper salts,** forming a small quantity of phosphide; and J. Nicklès found that a soln. of phosphorus in carbon disulphide precipitates the metal from soln. of copper salts. J. H. Gladstone noted the formation of phosphorus trichloride when yellow phosphorus acts on cupric chloride. T. Sidot showed that copper and copper phosphide are precipitated by yellow phosphorus from soln. of copper sulphate, and when all the copper has been precipitated from the soln., some hydrogen appears. J. W. Slater also observed the formation of copper, copper phosphide, and phosphoric acid when phosphorus acts on a soln. of copper nitrate. According to W. Straub, when phosphorus is placed in an aq. soln. of copper sulphate, it becomes black, and when removed from the soln. it does not react with the atm. oxygen. In the soln., the black coating becomes red on account of the deposition of metallic copper. Copper continues to be deposited as long as phosphorus is present, but in all cases the black deposit is first formed. This black substance is a copper phosphide, but its composition could not be accurately ascertained. As the reaction proceeds, the quantity of phosphoric acid in the solution continuously increases. The quantity of phosphorus which enters into reaction stands in a constant relationship to the amount of reduced copper sulphate only if the reaction is not carried to an end or if atm. oxygen is rigorously excluded. At the point where the reaction is just complete, the soln. contains sulphuric acid and phosphoric acid in the proportion 1 : 0·5, and consequently 1 mol. of phosphorus separates 2 mols. of copper from the copper sulphate soln. The oxygen which oxidizes the phosphorus must come from the water because the amount of sulphuric acid undergoes no diminution. The reduced copper is not acted on by the sulphuric acid, but is oxidized by the atm. oxygen, and the copper oxide dissolves to form copper phosphate, which is then reduced to phosphide. The dark film on the phosphorus is produced in a soln. containing only 1 gram-mol. of crystallized copper sulphate in 100,000 litres of water, and at a dilution 10 times as great the film is produced in the course of two months. F. Tauchert found hypophosphorous acid among the products of the reaction. J. B. Senderens found red phosphorus forms copper phosphide when in contact with a soln. of copper nitrate; and A. Granger, with a soln. of copper phosphite at 130°; and it also reacts with a soln. of copper chloride.

R. M. Bird and S. H. Diggs said that the main reaction of phosphorus on copper sulphate consists in the transfer of positive charges from copper ions to the phosphorus: $5Cu^{\cdot\cdot}+2P=2P^{\cdot\cdot\cdot\cdot\cdot}+5Cu$, and the immediate reaction of the phosphorus ions to form phosphoric acid. They found the ratio of the number of atoms of copper precipitated to those of phosphorus oxidized approximates 5 : 2. The phosphorus present as lower acids and phosphide is produced by secondary reactions. O. J. Walker showed that when a stick of phosphorus is placed in a soln. of a copper or silver salt, a reaction proceeds in two distinct stages. The first process is the formation of a black phosphide on the surface of the phosphorus; at the same time, the soln. is found to contain phosphorous acid. After a layer of the phosphide has been formed, metal begins to be deposited in a bright crystalline state, and phosphorus is oxidized to phosphorous and phosphoric acids. During this stage, approximately 4 eq. of the metals are deposited for every atom of phosphorus oxidized. The formation of a phosphide is due to the prior production of phosphine by the action of phosphorus on water, another portion of the phosphorus being simultaneously oxidized to phosphorous acid. This is evidenced by the exact parallelism which exists between the actions of phosphorus and phosphine on salt soln. of the heavy metals; only those metallic salt soln. which give phosphides by the action of phosphine are able to react with phosphorus. In confirmation, C. F. Cross and A. F. Higgins found that boiling water was decomposed by phosphorus, which was partly reduced to phosphine and partly oxidized to oxy-acids, and that, in the absence of oxygen, decomposition of the water took place only in the absence of certain metallic salts. O. J. Walker therefore suggests that the first stage in the action of phosphorus on the metallic salt takes place as follows (M and X representing an eq. of the positive and negative radicals, respectively): $2P+3H_2O=PH_3+H_3PO_3$, followed by $PH_3+3MX=PM_3+3HX$. The appearance of a deposit of the metal evidently depends on the preliminary formation of the phosphide. It has already been shown that the phosphides of silver and of other metals are capable of reacting with excess of the metallic salt to give the metal and phosphoric acid. The second stage, therefore, appears to be $M_3P+5MX+4H_2O=8M+5HX+H_3PO_4$. According to these equations, 4 eq. of the metal should be deposited for every atom of phosphorus oxidized, and this was the ratio actually obtained with silver and copper salts. The amount of phosphorous acid, however, was somewhat greater than that required by these equations. It is quite possible that this may be due to the following reaction proceeding to a small extent: $M_3P+3MX+3H_2O=6M+3HX+H_3PO_3$. This reaction consists essentially in the discharge of positive metal ions while phosphorus becomes oxidized, *i.e.* loses electrons. The ionic process may be represented as $M_3P+5M^{\cdot}=8M+P^{\cdot\cdot\cdot\cdot\cdot}$, the positive phosphorus ions reacting immediately with water to form phosphoric acid. According to this view, the $P^{\cdot\cdot\cdot\cdot}$-ions constitute an intermediate stage in the transition from phosphide to phosphoric acid. The discharge of $M^{\cdot}$-ions and the formation of $P^{\cdot\cdot\cdot\cdot\cdot}$-ions may occur at points widely separated from one another, provided that a metallic conducting path be available for the passage of the necessary electrons.

F. Wöhler, A. Vogel, W. Wicke, and R. Böttger found that ordinary phosphorus reduces soln. of **silver salts** to the metal, and W. Wicke, that a stick of phosphorus wrapped with silver wire and placed in a conc. soln. of silver nitrate gives in the course of a few weeks crystals of silver, while the phosphorus acquires a film of silver phosphide. J. Philipp showed that if phosphorus and silver nitrate soln. acidified with nitric acid be boiled, phosphorous and phosphoric acids and silver subphosphate are formed. T. Poleck and K. Thümmel found red phosphorus does not act on a conc. soln. of silver nitrate like yellow phosphorus, but it forms free acid and silver phosphide; J. B. Senderens represented the reaction: $2P+10AgNO_3+8H_2O=10Ag+2H_3PO_4+10HNO_3$—*vide supra*, for O. J. Walker's observations with copper and silver salts. L. Rosenstein found silver salts soln. are reduced to phosphide in a few minutes when boiled with red phosphorus. A. Granger observed no reaction between silver chloride and red phosphorus, similarly also with **gold chloride**; but L. Rosenstein found a few minutes' boiling with red phosphorus forms insoluble gold phosphide. B. Renault found that phosphorus vapour at a red-heat transforms **zinc carbonate** into zinc phosphides, and that it acts in an analogous way on **cadmium carbonate.** J. Nicklès also showed that a soln. of phosphorus in carbon disulphide precipitates zinc phosphide from soln. of **zinc salts.** L. Rosenstein found that cadmium salt soln. are not reduced by boiling with red phosphorus. A. Granger observed that red phosphorus does not react with **cadmium chloride** or with **mercuric chloride**; but if the soln. of a mercuric or mercurous salt is boiled a few minutes with red phosphorus, L. Rosenstein found that the salt is reduced to mercury. According to J. L. Gay Lussac and L. J. Thénard, yellow phosphorus forms phosphorus trichloride when it reacts with mercuric chloride; and C. Löwig observed that phosphorus bromide is formed when the vapour reacts with **mercurous or mercuric bromide.** F. Venturoli found that a yellow precipitate is formed when phosphorus acts on an alcoholic soln. of **mercuric iodide**: $6P+8HgI_2=4PI_3Hg_2+2PI_2$. A. J. Cenedella observed that yellow phosphorus becomes hot when mixed with **mercuric cyanide,** and, if an explosion does not occur, a white sublimate may be formed. A. Granger observed that when heated with **stannous sulphide,** red phosphorus forms the complex $SnP.2SnS$; analogous compounds are not produced with the sulphides of gold, cadmium, lead, or antimony. Red phosphorus does not react with **stannous chloride.** L. Rosenstein found **stannic salts** are partially reduced to stannous salts by a few minutes' boiling with red phosphorus; *but stannous salts* are not reduced. F. Wöhler, A. Vogel, W. Wicke, and R. Böttger found that **lead salts** are reduced by phosphorus to lead, and lead phosphide. W. Wicke found that when lead wire is wrapped on a stick of phosphorus, and immersed in a soln. of lead nitrate, a black film is deposited on the phosphorus, and lead crystals are formed. J. H. Gladstone observed no phosphorus trichloride is formed when phosphorus acts on lead chloride; and J. W. Slater found that when phosphorus is boiled with a soln. of lead nitrate, some lead phosphate is formed. L. Rosenstein found that soln. of lead salts are not reduced by boiling with red phosphorus.

G. Dragendorff showed that phosphorus reduces fused **borax** to boron; H. Moissan, that phosphorus reacts vigorously with **boron iodide**; W. Ramsay and R. W. E. MacIvor, that soln. of phosphorus and **antimony trichloride** in carbon disulphide form antimony phosphide. L. Rosenstein found that soln. of **permanganates** are reduced to manganous salts by a few minutes' boiling with red phosphorus; J. W. Slater observed that potassium permanganate soln. is reduced by yellow phosphorus to manganese dioxide; **potassium chromate and dichromate** at ordinary temp. slowly form chromium phosphate; **copper chromate** forms copper, copper phosphide, chromium phosphate, and phosphorous and phosphoric acids; but **lead chromate** is scarcely affected when boiled with phosphorus. E. Kopp noticed that potassium dichromate soln. is reduced by phosphorus in sunlight, or by warmth; and A. Stiassny found that when phosphorus is burnt under a bell-jar in the presence of a soln. of potassium dichromate, some of the dichromate is reduced, possibly owing to the formation of hypophosphorous acid. A. Schrötter said an aq. soln. of potassium dichromate does not act on red phosphorus; but combustion occurs when the dry salt is triturated or heated with red phosphorus. L. Rosenstein also found that soln. of dichromates are reduced to chromic salts by a few minutes' boiling with red phosphorus; under similar conditions, **molybdates** form quadrivalent molybdenum salts; and **vanadates,** tervalent vanadium salts. A. Granger found that red phosphorus reacts with **nickel chloride, cobalt chloride,** and with **ferric chloride**; and J. H. Gladstone showed that with yellow phosphorus, ferric chloride forms phosphorus trichloride. I. W. Schmoss found that on boiling an alcoholic soln. of **nickel nitrate,** sat. at 20°, with yellow phosphorus, a pale green precipitate of nickel triphosphate, $NiH_3P_3O_{10}.3H_2O$, is formed. L. Rosenstein found ferric salt soln. are reduced to ferrous salts by a few minutes' boiling with red phosphorus; **palladium salts** and **osmium salts** are reduced to metal or phosphide; **iridic salts** to iridous salts; but **chloroplatinates** are but slowly reduced.

The physiological action of phosphorus.—Yellow phosphorus was formerly used largely in the preparation of lucifer matches, and the workman exposed to the fumes suffered from necrosis or rotting of the bones of the upper and particularly of the lower jaw—*phossy-jaw*. The use of red phosphorus and improved hygienic conditions have done much to minimize the risks of chronic phosphorus poisoning.

Phosphorus vapour or rather that of phosphorus oxide—*vide supra*—acts locally on bone tissue wherever it is exposed; so long as it is covered with mucous membrane, the bone is not attacked. The vapour finds its way to the bone through decayed teeth, or the space left where a tooth is absent. The bone is first attacked with periostitis, and then with necrosis, which may spread far from the point originally attacked. The general health is then broken down. In healthy subjects, apart from its action on exposed bone, phosphorus vapour in the atm. of a match factory is not considered to be a toxic agent; the phosphorus absorbed is largely eliminated with the urine, and there may be slight albuminuria with no other perceptible pathological disturbance.

Acute phosphorus poisoning occurs when mixtures containing phosphorus are swallowed—*e.g.* vermin-killers or rat-pastes; and match-heads made with yellow phosphorus—through an accident, as when children suck and swallow the heads of matches, when a phosphorus rat-paste, or a mixture of match-heads and water is swallowed as a means of committing suicide, or with the object of procuring abortion by pregnant women. Finely-divided phosphorus can be absorbed as such without previously being oxidized. Immediately after swallowing, a disagreeable taste may be experienced; there may be intense pains in the throat, gullet, and stomach; retching and vomiting may follow; the throat and tongue may swell; and the breath may become phosphorescent. These preliminary symptoms may be delayed a number of hours. Gastro-intestinal irritation occurs—nausea, abdominal pain, and vomiting; the vomited matters may smell of phosphorus and be luminescent. There may be general depression; diarrhœa is rare. The subject may die of collapse, or may apparently recover; but in a few days, jaundice appears. General prostration follows, the liver is enlarged, and the abdomen distended. There may occur frequent vomiting of altered blood, diarrhœa with bloody stools, skin affections, retention of urine, sleeplessness, and headache. There may follow acute delirium and fever, coma, and death, or coma may set in and death follow in sleep without delirium. A. Tardieu[12] said that acute poisoning by phosphorus is sometimes rapid, sometimes slow; and the symptoms may take three distinct forms—a common form, a nervous form, and a hæmorrhagic form. In certain cases, these three forms may succeed each other, and may only constitute periods of poisoning; but each may show itself alone, and occupy the whole course of the illness produced by the poison. In the nervous form, there are strange creeping sensations about the limbs, painful cramps, repeated faintings, great somnolence, jaundice, acute delirium, lockjaw, convulsions, and death. In the hæmorrhagic form there is a great effusion of blood—nose, mouth, bladder, kidneys, and bowels. The liver swells, and is painful; there is great bodily weakness, and death may occur months after the poison has been taken. Recovery from phosphorus poisoning has occurred after 4–6 grains have been taken in the form of rat-poison, but 1½ grains have proved fatal.

In phosphorus poisoning, the proportion of blood corpuscles is increased. Numerous investigations have been reported on the subject. In general, the phosphorus stimulates metabolic changes as shown by the increased proportion of sulphates, phosphates, and nitrogen in the urine. The nitrogen comes from the excess of ammonia formed in the protein tissues; and appears in the blood neutralizing the lactic and acetone acids which appear in the blood because the phosphorus prevents the complete oxidation of glycogen, fat, and other non-nitrogenous products from the breaking down of the proteins. The fat is partially deposited in the liver and muscles and leads to fatty degeneration of the tissues. R. Schenck found that scarlet phosphorus is not poisonous; and M. de Vrij, and A. Postans, that dark red phosphorus is likewise non-toxic. H. Köhler and H. W. Schimpf, and L. E. Jonas said that turpentine is an antidote for phosphorus poisoning because it produces an inert complex, but V. Plavec denied the effectiveness of the alleged antidote. J. Stoklasa[13] and co-workers, O. Loew, H. Schmidt, T. Bokorny, M. Tsvett, and F. Scurti studied the action of phosphorus on plants.

The uses of phosphorus.—Phosphorus is employed in making bronzes, and for hardening alloys,[14] when it is added in the form of copper phosphide; it is used in gas analysis; and it has been used to a small extent medicinally as *oleum phosphoratum*—a soln. of one part of phosphorus in 98 of almond oil—and as *pilula phosphori*—a mixture of china clay, fat, and theobroma oil with one per cent. of phosphorus. Yellow and red phosphorus are chiefly employed in making matches. H. W. Walker discussed its use in making smoke screens.

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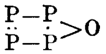
§ 8. The Atomic Weight and Valency of Phosphorus

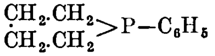
Phosphorus behaves both as a tervalent and as a quinquevalent element. As with nitrogen in ammonia, NH_3, phosphorus in phosphine, PH_3, is clearly tervalent, and all attempts to isolate phosphonium, PH_4, analogous with ammonium, NH_4, have proved abortive. In phosphorus trichloride, PCl_3, the element is tervalent, but F. A. Kekulé[1] argued that in phosphorus pentachloride, PCl_5, phosphorus is still tervalent, and that the pentachloride is a molecularly associated compound, $PCl_3.Cl_2$, because when heated, the molecule is dissociated: $PCl_5 = PCl_3 + Cl_2$. A. Wurtz, however, showed that if an excess of trichloride be present, the pentachloride can be vaporized without decomposition: and H. B. Baker's work showed that if the thoroughly dried pentachloride were vaporized its dissociation would be inappreciable. All this means that F. A. Kekulé's hypothesis is untenable, and that the phosphorus is quinquevalent in the pentachloride, as T. E. Thorpe showed to be the case with the pentafluoride which can be vaporized without decomposition. Following on the same argument, phosphorus appears to be septavalent in E. Baudrimont's hexachloroiodide, PCl_6I, and in A. Michaelis' trichlorotetrabromide, PCl_3Br_4; and undecivalent in M. Prinvault's and Michaelis' trichloroctobromide, PCl_3Br_8. The difficulty is here overcome by assuming, as in the analogous case of nitrogen, that the valencies of the halogens are greater than unity, so that the maximum valency of phosphorus is five. From the thermochemical data, J. C. Thomlinson argued that phosphorus is quadrivalent. A. A. Blanchard assumed that the non-polar valency of phosphorus in its pentachloride is five. A. Bilecki, A. P. Mathews, T. M. Lowry, H. Goldschmidt, and R. De discussed the valency of phosphorus.

The molecular formulæ of the tri- and pent-oxides are respectively P_4O_6 and P_4O_{10} as shown respectively by T. E. Thorpe and A. E. H. Tutton, and by W. A. Tilden and R. E. Barnett. It is assumed that the phosphorus in the trioxide is tervalent because hydrogen chloride converts the oxide into phosphorous chloride, PCl_3, and phosphorous acid, $P(OH)_3$; while phosphorus in the pentoxide is assumed to be quinquevalent because water converts the oxide into phosphoric acid, $O : P(OH)_3$. Since water converts phosphorus tetroxide, P_2O_4, into a mixture of phosphorous and phosphoric acids, it has been argued that one phosphorus atom is tervalent, and the other quinquevalent. In the alleged phosphorus tetritoxide, P_4O, of A. Michaelis, the phosphorus is assumed to be tervalent:



$$\begin{array}{c}P-P\\ \vdots\quad\vdots\\ P-P\end{array}\!>O$$

Two isomers with the empirical formula $(C_6H_5)_3PO$, were prepared by A. Michaelis and W. la Coste. The properties of neither agree with the formula $P(C_6H_5)_2.C_6H_4.OH$. The one—phenoxydiphenylphosphine—prepared by the action of diphenylchlorophosphine on phenol, $(C_6H_5)_2PCl+C_6H_5OH=HCl+(C_6H_5)_2P.O.C_6H_5$, is a thick, oily liquid; and the other—triphenylphosphine oxide—prepared by the action of water on triphenylbromophosphine bromide, $(C_6H_5)_3PBr_2+H_2O=2HBr+(C_6H_5)_3P : O$, is solid with the m.p. 153·5°. With this interpretation, phosphorus is tervalent in the one case and quinquevalent in the other. In the *cyclo*-tetramethylenephenyl phosphine



$$\begin{array}{l}CH_2.CH_2\\ CH_2.CH_2\end{array}\!>P-C_6H_5$$

of E. Krause, the phosphorus forms the fifth member of a heterocyclic system.

Assuming that the sp. vol. of phosphorus is constant, T. E. Thorpe argued that the phosphorus in phosphoryl chloride, $POCl_3$, must be tervalent, and the molecule unsymmetrical, $Cl.O.PCl_2$, and not $O : PCl_3$; but W. Ramsay and D. O. Masson showed that the assumption is not justified, for evidence, deduced from other elements, indicates that there is a change of sp. vol. in passing from singly to doubly linked atoms. R. M. Caven tried to demonstrate that the three valencies of tervalent phosphorus lie in one plane as in the analogous case of nitrogen; and he inferred that the centres of gravity of the three chlorine atoms lie at the angles of an equilateral triangle; and if an imaginary line is drawn through the centre of this triangle and at right angles to its plane, the centres of gravity, both of the phosphorus atom and of the oxygen atom are situated in this line. The question whether the phosphorus atom lies in the same plane as the three chlorine atoms remains undecided. The expectation that phosphorus should yield optically active derivatives, as in the case of nitrogen, has not been realized. R. M. Caven, and A. Michaelis were unable to obtain activity with compounds of the type: $PR_1R_2R_3R_4X$—and the latter thinks it possible that the failure was due to the poisonous action of the compounds on the ferments employed; but L. Lichtenstadt obtained $(CH_3)(C_2H_5)(C_6H_5)(C_6H_5.CH_2)PI$, as a bromocamphor sulphonate, which was dextrorotatory. J. Meisenheimer and L. Lichtenstadt prepared optically active phenylmethylethylphosphine oxide, $O : P(CH_3)(C_2H_5)(C_6H_5)$.

A. L. Lavoisier's[2] measurement of the increase in weight which occurs when phosphorus is fully oxidized corresponded with an at. wt. 28 (oxygen, 16); H. Davy's, 26·2; T. Thomson's, 24·5; and V. Rose's, 35. J. J. Berzelius at first gave 26·8, and later 31·36. The value approximating 31 is in harmony with the gas density law, the sp. gr. rule, the law of isomorphism, and the periodic law. J. J. Berzelius' value 26·8 was obtained from the analysis of the phosphates; and from the ratio 3P : 5Au obtained by precipitating gold from soln. of its salts by phosphorus he calculated the at. wt. 31·56, and from the ratio P : 5Ag, 31·32. P. L. Dulong obtained the erroneous result 27·3 from the ratio P : PCl_3; J. Pelouze, 32·3 from the ratio PCl_3 : 3Ag obtained by titrating phosphorus trichloride with a standard soln. of silver nitrate, while V. A. Jacquelain did even worse, obtaining from 19·7 to 48·7—results which A. Schrötter proved to be quite valueless. A. Schrötter burnt phosphorus in oxygen, and from the ratio 2P : P_2O_5, calculated 31·03 for the at. wt. of phosphorus; J. B. A. Dumas titrated phosphorus trichloride with silver nitrate, and calculated from the ratio PCl_3 : 3Ag, 31·04; J. D. van der Plaats from the ratio P : 5Ag, obtained by treating a soln. of silver nitrate with phosphorus, calculated 30·93; from the ratio Ag_3PO_4 : 3Ag, 30·99; and from the ratio 2P : P_2O_5 obtained by oxidizing phosphorus, he calculated 30·98. G. P. Baxter and G. Jones calculated 31·02 from the ratio 3AgBr : Ag_3PO_4, with the at. wt. of silver 107·86. G. Ter-Gazarian measured the density of phosphine, and hence calculated for the at. wt. of phosphorus 30·098. Considering all the available reliable determinations, F. W. Clarke gave 30·925 as the best representative value; B. Brauner, 31·0; while the International Table for 1925 gives 31·027.

The **atomic number** of phosphorus is 15. According to F. W. Aston,[3] there is only one **isotope** of phosphorus with an at. mass 31. E. Rutherford and J. Chadwick, F. Chalfin, G. Kirsch, and G. Kirsch and H. Pettersson, found evidence of **atomic disintegration** when the atoms of phosphorus are bombarded by α-particles from radium. N. Bohr represents the **electronic structure** of the atom, to show the number of electrons in the different orbits thus: (2) (4, 4) (2, 2, 1). C. G. Bedreag, H. Collins, L. Brüninghaus, T. M. Lowry, J. H. W. Booth, J. H. Jones, H. G. Grimm and A. Sommerfeld, H. Lessheim and R. Samuel, C. D. Niven, M. L. Huggins, B. Rosen, R. H. Ghosh, S. C. Biswas, and H. Burgarth made observations on the electronic structure of the phosphorus atom.

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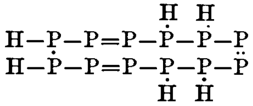
§ 9. Hydrogen Tritaphosphide, or Phosphorus Trihydride, or Phosphine

The action of hydrogen on phosphorus, and I. Langmuir's[1] observation that activated or atomic hydrogen reacts directly with phosphorus, forming phosphine, have been previously discussed. In 1783, P. Gengembre discovered that when phosphorus is boiled with a soln. of sodium or potassium hydroxide, a gas is evolved which is spontaneously inflammable when exposed to air; he called it *gas phosphorique inflammable.* Soon afterwards, but independently, R. Kirwan obtained the gas in a similar way; he called it *phosphatic hepatic air;* and considered it to be "phosphorus in an aerial state." In 1792, J. M. Raymond prepared it by heating phosphorus with slaked lime; and next year, G. Pearson obtained it by the action of water on the calcium phosphide obtained by heating quicklime with phosphorus in a luted vessel. In 1790, B. Pelletier had obtained a gas not spontaneously inflammable in air by the action of heat on phosphorous acid. There were thus two "phosphatic airs," and the text-books about that time—*e.g.* C. Girtanner, *Anfangsgrunde der antiphlogistischen Chemie* (Berlin, 1792)—called the gases *phosphuretted hydrogen.* The nature of the gas was established by H. Davy, who showed that its composition is analogous with that of ammonia. The compositions of the spontaneously inflammable gas, and the one which does not so inflame, were the same. P. Thénard showed that the cause of the spontaneous inflammability of the gas in air is due to the presence of a different phosphorus hydride as impurity. This constituent is liquid at ordinary temp. In 1826, J. B. A. Dumas showed that while the non-spontaneously inflammable gas has the empirical composition PH_3, or **hydrogen tritaphosphide**—commonly called **phosphine**—the empirical composition of the spontaneously inflammable constituent is PH_2, or **hydrogen hemiphosphide,** P_2H_4, *i.e.* $(PH_2)_2$. U. J. J. Leverrier in 1835 discovered a solid phosphorus hydride, which he represented by the formula PH, but P. Thénard showed that it is a **hydrogen diphosphide,** P_4H_2, or $(P_2H)_2$, or, according to A. Stock and co-workers, $P_{12}H_6$, *i.e.* $(P_2H)_6$, and H. Henstock assumed that this compound contains tervalent phosphorus, alternately + and —, with the ring structure:



$$\begin{array}{ccccccccccccc} &&&&&&&&\mathrm{H}&&\mathrm{H}&& \\ &&&&&&&&\cdot&&\cdot&& \\ \mathrm{H}&-&\mathrm{P}&-&\mathrm{P}&=&\mathrm{P}&-&\mathrm{P}&-&\mathrm{P}&-&\mathrm{P} \\ &&\cdot&&&&&&&&&&\cdot\cdot \\ \mathrm{H}&-&\mathrm{P}&-&\mathrm{P}&=&\mathrm{P}&-&\mathrm{P}&-&\mathrm{P}&-&\mathrm{P} \\ &&&&&&&&\cdot&&\cdot&& \\ &&&&&&&&\mathrm{H}&&\mathrm{H}&& \end{array}$$

These workers also obtained **hydrogen hemienneaphosphide,** P_9H_2, by the action of heat on the diphosphide. L. Hackspill also reported the solid **hydrogen hemipentaphosphide,** P_5H_2, to be formed by heating the hemienneaphosphide in vacuo at 80°, or by the action of dil. acetic acid on the corresponding alkali phosphides.

Some other hydrogen phosphides have been reported. Thus, T. A. Commaille[2] supposed *hydrogen triphosphide,* P_3H, to be formed by the action of aq. ammonia of sp. gr. 0·971, on ordinary, but not on red phosphorus; but this has not been confirmed—*vide supra*, action of aq. ammonia on phosphorus. N. Blondlot said that red phosphorus is produced by the action of ammonia on ordinary phosphorus; and F. A. Flückiger, that an ammine of phosphorous oxide is formed. G. Janssen also reported a crystalline *hydrogen ditritaphosphide*, P_2H_3, to be formed in hexagonal prisms when phosphorus is boiled with milk of lime. This report has not been verified.

The curious natural phenomenon known as *ignis fatuus* (*ignis*, fire; *fatuus*, wild, silly), or in France *feux follets*, often manifests itself as a more or less transient, flickering, " light, spirituous flame dancing on the heath," and it has been frequently reported to appear in darkness over peat-bogs, swamps, marshy districts, lagoons, damp cemeteries, recent battle-fields, stagnant waters, etc. The *ignes fatui* were at one time thought to be manifestations of the supernatural, and were called in Scotland *elf-candles* or *elf-fire*—in allusion to the elves or mischievous sprites which the superstitious believe haunt the wild places where the phenomenon usually occurs; in Wales, *corpse-candles*—in reference to their frequent appearance in cemeteries; and in England, *Jack-o'lanterns* or *Will-o'the-wisps*—in allusion to rustic fairy tales. Some rather brilliant displays have been reported at various times. The phenomenon is not to be confused with the light from luminous insects hovering over marshy grounds. The general idea is that the *ignes fatui* are due to the spontaneous ignition of bubbles of gas containing traces of phosphuretted hydrogen evolved, along with other gases, during the decomposition of animal substances under water or in damp soils. Bubbles of gas no doubt escape in the day as well as at night, but the feeble light which is emitted when a gas bubble containing a little phosphuretted hydrogen comes in contact with the air, is visible only in dusk or in darkness. In support of this B. von Dybkowsky [3] said that phosphine is produced when dried blood or gastric juice is kept at 35°–41° for a long time; and A. Gautier and A. Étard, that it is produced during the putrefaction of proteins. E. Pozzi-Escott observed that the hydrogenation of phosphorus to phosphine occurs when hydrogenases act by diastatic fermentation on the element. J. N. Lockyer found phosphine amongst the gases expelled when some minerals are heated in vacuo. W. Steffens reported that the mortar in one part of an old building gave phosphine on treatment with water. The phosphine is said to have been derived from calcium phosphide thought to have been formed from the calcium phosphate originally present, being reduced electrolytically from a short circuit.

The formation and preparation of phosphine.—The modes of preparation are sometimes divided into (i) those which furnish the spontaneously inflammable gas, *i.e.* the gas inflames when it comes in contact with air at ordinary temp. and press.; and (ii) those which furnish the non-spontaneously inflammable gas which takes fire only at an elevated temp. or under a reduced press. Since these divergent qualities are determined by the presence or absence of traces of hydrogen hemiphosphide, $(PH_2)_2$, and since this impurity may or may not be removed from the gas by suitable treatment, there are no essential differences in the modes of preparation of the spontaneously accendible and non-accendible forms of the gas. T. Graham [4] made a special study of the conversion of the spontaneously inflammable gas into the non-accendible form. He said:

> The accendible form of the gas passes into the other one when it is confined over water containing air—no phosphorus is produced during the conversion—the presence of cork or gypsum with air in their pores suffices for the conversion. The presence of about 5 vols. of hydrogen; 2 vols. of carbon dioxide; 1 vol. of ethylene; 0·5 vol. of hydrogen sulphide; 0·2 vol. ammonia; 0·1 vol. nitric oxide; 0·05 vol. hydrogen chloride per vol. of phosphine destroys the spontaneous inflammability of the gas—the mixture with 0·1 vol. of nitric oxide gives red fumes in air, and a mixture with 0·05 vol. of nitric oxide takes fire with a kind of detonation while the bubble is rising in air. When the sides of the containing vessel are moistened with conc. phosphoric, sulphuric, or arsenic acid, the conversion occurs in 2–3 minutes and the change is attended by a mutual decomposition. Arsenious acid acts quickly, so does mercurous oxide; but potash-lye requires some hours to do the work. Potassium alone, or in the form of an amalgam with one part of

potassium in 350,000 parts of mercury, destroys the spontaneous inflammability in a few minutes. Freshly ignited charcoal quenched in mercury, not water, adsorbs a large proportion of the gas but renders the remainder not spontaneously inflammable in half an hour ; when the charcoal is heated, the evolved gas is the non-accendible form ; burnt clay acts similarly. Spongy platinum, mercuric oxide, and a soln. of ferrous sulphate do not destroy the quality.

J. B. A. Dumas thought that the gas which is readily accendible has the composition PH_3, and that which is not so, the composition PH_2 ; but H. Rose showed that this hypothesis is wrong ; the density and composition of both gases are the same. T. Graham concluded that the spontaneous inflammability is due to the presence of some impurity—probably a lower oxide of phosphorus, not nitrogen trioxide. U. J. J. Leverrier said that the impurity is probably another hydrogen phosphide—P_2H_4—and P. Thénard proved that this hypothesis is probably correct, although M. Bonet y Bonfil tried to show that the inflammability is probably due to the presence of phosphorus in both gases but in different states. J. W. Retgers, D. Amato, etc., established the original suggestion of U. J. J. Leverrier, and P. Thénard.

The most difficult impurity to eliminate is hydrogen, which is nearly always formed simultaneously with the phosphine. G. Ter-Gazarian found the most effective method of purifying the gas from traces of other hydrogen phosphides, and from hydrogen is repeated liquefaction and fractional distillation of the liquid. F. M. G. Johnson recommended alumina, dehydrated at a low temp., as a desiccating agent for the gas.

The impure, spontaneously inflammable gas was prepared by P. Gengembre by boiling a conc. soln. of potassium hydroxide with yellow phosphorus. A similar process was employed by R. Kirwan, J. B. A. Dumas, T. Weyl, T. A. Commaille, R. Schenck, H. Rose, and F. Brandstätter. The reaction was studied by H. Rose, who found that some gas is given off even at 15°. The main reaction taking place when yellow or red phosphorus is boiled with potash-lye results in the formation of potassium hypophosphite and phosphine: $4P+3KOH+3H_2O=3KH_2PO_2+PH_3$, some hydrogen hemiphosphide is formed by a side reaction: $6P+4KOH+4H_2O=4KH_2PO_2+P_2H_4$; part of the hemiphosphide may decompose into the diphosphide, $15P_2H_4=P_{12}H_6+18PH_3$. Much free hydrogen is associated with the phosphine. According to J. B. A. Dumas, it is difficult to make phosphine by this process without, say, 60 per cent., or, according to A. W. Hofmann, 55 per cent. of hydrogen : $2P+2KOH+2H_2O=2KH_2PO_2+H_2$; less hydrogen is formed the greater the conc. of the alkali-lye. According to P. L. Dulong, near the end of the reaction, more hydrogen is formed by the oxidation of the hypophosphite to phosphate : $KH_2PO_2+2H_2O=KH_2PO_4+2H_2$, and to pyrophosphate: $2KH_2PO_2+3H_2O=4H_2+K_2H_2P_2O_7$. It has also been suggested that potassium phosphide, K_3P, and phosphorous acid, $P(OH)_3$, are first produced : $4P+6KOH\rightarrow 2K_3P+2P(OH)_3$; and that the phosphorous acid reacts with the excess of potassium hydroxide always present, forming potassium monohydrogen phosphite : $2P(OH)_3+4KOH\rightarrow 2K_2HPO_3+4H_2O$, while the potassium phosphide reacts with water: $2K_3P+7H_2O\rightarrow PH_3KH_2PO_2+5KOH+2H_2$. The main action of phosphorus on boiling potash-lye is then symbolized by combining these equations into one: $4P+5KOH+3H_2O\rightarrow PH_3+2H_2+KH_2PO_2+2K_2HPO_3$. T. von Grotthus regarded the mixture of gases produced by the action of potash-lye on phosphorus as a special gas which he called *Phosphorkohlenwasserstoff gas*. Other alkali hydroxides can be used. W. R. Hodgkinson said that the reaction is not hindered by glycerol. In place of alkali-lye, J. M. Raymond used dry calcium hydroxide, but H. Rose showed that a greater proportion of hydrogen is then formed ; and J. B. A. Dumas, using milk of lime in place of alkali-lye, obtained a gas with 89–90 per cent. of free hydrogen. Hydroxides of the other alkaline earths, or of zinc or iron (ous), can be used. The following is a modernized form of P. Gengembre's experiment :

A conc. soln. of sodium or potassium hydroxide and yellow phosphorus is placed in the flask fitted with delivery tube, etc. A current of an inert gas—coal gas, hydrogen, or carbon dioxide—is first led through the apparatus to drive out the air; or, as recommended by F. Brandstätter, a few drops of ether are introduced into the flask, and as this vaporizes it drives out the air. If the temp. of the mixture be raised very slowly the expulsion of the air in this way is not necessary since the oxygen is removed by the first bubbles of phosphine. E. Löwenhardt fills the generating flask to within "4 c.c." of the stopper. The mixture in the flask is then heated. The phosphorus reacts with the alkali-lye, forming alkali hypophosphite, and gaseous phosphine, associated with some impurities. The mixture of gases so prepared is sometimes called *phosphuretted hydrogen.* Each bubble of gas rises to the surface of the water, and, when it comes in contact with the air, ignites with a slight explosion and burns with a brilliant flash of light, forming a vortex ring of phosphorus pentoxide.

The degree of the spontaneous inflammability of phosphine depends upon the conditions under which the gas has been prepared. In all methods for making phosphine, excepting the phosphonium halide process, A. W. Hofmann found that the gas may contain up to 90 per cent. of hydrogen, while the action of potash-lye on yellow phosphorus gave a gaseous mixture of phosphine with 60 to 90 per cent. of hydrogen, conc. alcoholic potash-lye gave a mixture with 55 per cent. of hydrogen. It does not appear possible to prepare a gas with more than 50 per cent. phosphine by the action of aq. or alcoholic potash-lye on phosphorus. H. Rose showed that the gas obtained by the action of alcoholic potash-lye on yellow phosphorus is mixed with hydrogen and alcohol, and is not usually spontaneously inflammable; and W. R. Hodgkinson showed that an alcoholic soln. of sodium ethoxide acts on yellow phosphorus, giving a fairly pure gas which is not spontaneously inflammable. P. Thénard, and D. Amato showed that phosphuretted hydrogen loses its property of spontaneously inflaming in air if it be treated with conc. hydrochloric acid, or exposed to sunlight. The contained hemiphosphide is thereby decomposed.

Phosphine is obtained by the action of water or dil. acids on the phosphides of the alkalies or alkaline earths. P. Thénard made phosphine by the action of water or dil. acids on the phosphides of the alkalies; and A. Joannis, by the action of water or heat on the dihydromonophosphides, *e.g.* KPH_2 or $NaPH_2$. The reaction between water and, say, sodium phosphide is probably more complex than is represented by the equation: $Na_3P+3H_2O=PH_3+3NaOH$, because some hypophosphite and phosphite appear among the products of the reaction; W. P. Winter suggested the complex equation: $4Na_3P+14H_2O=2PH_3+NaH_2PO_2$. The formation of the spontaneously inflammable gas is explained by assuming that the normal phosphide is contaminated with some of the hemiphosphide. C. Hugot obtained phosphine by the action of water or dil. acids on sodium trihydrodiphosphide, $Na_3H_3P_2+3H_2O=3NaOH+2PH_3$, or $Na_3H_3P_2+3HCl=3NaCl+2PH_3$; or by heating the same substance to 100° under reduced press. At higher temp. more hydrogen and less phosphine is produced until at 200°–300° only phosphine appears. W. P. Winter found that phosphine is produced by the action of water on the chocolate brown substance obtained by treating sodamide with yellow phosphorus. G. Pearson, P. Thénard, C. Matignon and R. Trannoy, B. König, T. Thomson, and R. Lüpke prepared phosphine by the action of water or dil. acid on calcium phosphide. H. Moissan found that calcium phosphide made by heating calcium phosphate in an electric furnace yields a fairly pure phosphine. As H. Rose has shown, some solid hydrogen phosphides are produced when the phosphides of the alkalies or alkaline earths are treated with acids. J. B. A. Dumas said that when barium phosphide is used, 43 per cent. of hydrogen may be present; with calcium phosphide and water, 13 per cent.; and with calcium phosphide and dil. hydrochloric acid, 7 per cent. of hydrogen is present at first, and later, 13 per cent. H. Buff obtained a similar result with calcium phosphide and water; and A. W. Hofmann said it is very difficult by this process to obtain a gas free from hydrogen. R. Lüpke found that phosphine is obtained by the action of water or dil. acids on magnesium phosphide;

H. Schwarz, P. Jolibois, F. Brandstätter, H. Rose, and R. Lüpke used zinc, tin, or iron phosphide and dil. sulphuric or hydrochloric acid; P. Kulisch used cadmium phosphide and dil. acids; P. Kulisch, cadmium phosphide; H. Fonzes-Diacon, C. Matignon, and F. Bodroux, aluminium phosphide; and R. Lüpke, *copper phosphide*, and iron phosphide—in both cases the reaction is slow, but R. Böttger used an alcoholic soln. of potassium cyanide and obtained a larger yield. A. W. Hofmann found that the gas is accompanied by variable amounts of hydrogen. According to F. Bodroux, temp. is a controlling factor in determining the amount of hydrogen obtained from the decomposition of the phosphides by water. Magnesium and aluminium phosphides, when decomposed by iced water, slowly give off phosphine with hydrogen; but when the temp. exceeded 50° or if acids were employed, the phosphine was contaminated with much hydrogen. H. Blumenberg obtained the nascent hydrogen, for the production of phosphine, electrolytically.

W. Ipatieff and W. Nikolaieff observed the formation of phosphine when white phosphorus is heated with hydrogen in a sealed tube at 360°; and when water-gas at 400 atm. press. acts on lead phosphate. J. Brössler said that if white phosphorus be added to a mixture of zinc and dil. sulphuric acid, in a short time, spontaneously inflammable phosphine will be produced; and if a conc. soln. of alkali hydroxide and zinc be mixed with yellow phosphorus, the spontaneously inflammable gas will be given off at about 60°; if the temp. be below 20°, the gas evolved is not spontaneously inflammable. H. Davy, and L. Dusart showed that the gas obtained by the action of zinc and dil. acids on yellow phosphorus contains phosphine, although J. B. A. Dumas questioned the fact. D. Vitali observed that the presence of mercuric chloride retards the formation of phosphine. J. Brössler obtained phosphine by the action of hydrochloric acid and a few drops of nitric acid on tin in the presence of yellow phosphorus. The formation of phosphine during the action of ammonia, and of water on yellow phosphorus has been indicated in connection with the chemical reactions of phosphorus.

According to A. Oppenheim, phosphine is formed when red phosphorus is heated in a sealed tube with conc. hydrochloric acid at 600°, possibly by the reactions $3HCl+2P=PH_3+PCl_3$; and $PCl_3+3H_2O=H_3PO_3+3HCl$. Hydrobromic acid acts more slowly than hydrochloric acid; and with hydriodic acid, the sealed tube can be heated to 160°. A. Oppenheim also heated phosphorus with syrupy phosphoric acid in a sealed tube at 200°, and found that hypophosphorous acid is formed which passes into phosphine and phosphoric acid. T. Weyl represented the action of hydrogen dioxide on red phosphorus by $6H_2O_2+4P=4P(OH)_3$; and $4P(OH)_3=PH_3+3H_3PO_4$; and C. A. Lobry de Bruyn noticed the smell of phosphine when hydrazine hydrate acts on yellow phosphorus. W. B. Grove also obtained a little phosphine by passing an electric current through moist molten phosphorus; if under reduced press., no phosphine is formed, presumably owing to the removal of the moisture. U. J. J. Leverrier observed that phosphine is formed when phosphorus tetritoxide is treated with conc. potash-lye; and B. Reinitzer and H. Goldschmidt, H. Biltz, and A. Michaelis and M. Pitsch obtained a similar result. B. Pelletier, and H. Davy obtained phosphine by heating phosphorous acid, and P. L. Dulong, H. Rose, J. B. A. Dumas, and A. W. Hofmann by heating hypophosphorous acid: $4H_3PO_2=2PH_3+2H_3PO_4$. According to J. J. Berzelius, phosphine is also formed when aq. soln. of phosphites are reduced by zinc or iron; F. Wöhler used zinc with a mixture of phosphorous and sulphuric acids. A. W. Hofmann found that pure phosphorous acid gave a gas with 6 per cent. of hydrogen. R. Lüpke obtained phosphine when phosphites or hypophosphites are reduced by nascent hydrogen. H. Rose said that when alkali hypophosphite is heated the spontaneously inflammable gas evolved may be readily inflamed or it may inflame with difficulty—this, said C. F. Rammelsberg, depends on *ganz zufälligen Umständen.* H. Rose added that the gas is accompanied by hydrogen and the vapour of phosphorus. Contrary to W. Herapath's statement, R. Fresenius said that the phosphates are not reduced by nascent hydrogen, but W. A. Ross maintained that metaphosphates are reduced to phosphine when heated with zinc.

According to G. S. Sérullas, the gas obtained by decomposing phosphonium bromide with water is of a high degree of purity ; and, according to A. W. Hofmann, the best process for phosphine of a high degree of purity is to treat phosphonium iodide with water :

Phosphine is made by mixing pieces of phosphonium iodide the size of a pea with pieces of glass in a flask. The flask is closed with a 2-hole rubber stopper carrying a stoppered-funnel and a delivery tube. A soln. of potassium hydroxide in twice its weight of water is added from the stoppered funnel very slowly. No heating is necessary. If the potash-lye be added too quickly the gas may be self-accendible owing to its containing some liquid hydride ; the gas at the end of the operation is also liable to be self-accendible. The reaction is symbolized: $PH_4I+KOH \rightarrow H_2O+KI+PH_3$. Ten grams of phosphonium iodide will give from 1·3 to 1·4 litres of the gas. Water can be added instead of potash-lye ; a 100 c.c. gas generating flask containing 20 grms. of phosphonium iodide, is fitted with a two-holed rubber stopper. One tubulure holds a stoppered funnel with a capillary tube bent so as to direct the stream of water to the side of the flask, and not directly on the iodide. The gas passes through conc. hydrochloric acid to remove liquid phosphide ; through conc. potash-lye to remove hydrogen chloride and iodide ; over calcium chloride and phosphorus pentoxide to dry the gas. J. Messinger and C. Engels say that it is best to mix the phosphonium iodide with ether, and add water from the separatory-funnel.

M. Bretschger, and B. Lepsius prepared the gas by this process; and C. F. Rammelsberg reported that even here the product may be spontaneously inflammable in air. P. de Wilde found the gas among the products of the action of phosphonium iodide on phosphorus tribromide ; E. and P. Fireman, among the products of the action of antimonic or stannic chloride on phosphonium iodide ; and R. Boulouch, among the products of the action of conc. potash-lye on phosphorus tetritaiodide. A. Stock and co-workers said that small quantities of fairly pure phosphine can be readily obtained by heating the diphosphide, $P_{12}H_6$, under reduced press. T. E. Thorpe and A. E. H. Tutton obtained phosphine by dissolving diamidophosphorous acid, $P(OH)(NH_2)_2$, in dil. hydrochloric acid. A. C. Vournasos showed that phosphine can be prepared by heating sodium formate at 200° in an atm. of hydrogen and phosphorus vapour: $6HCOONa+2P=2PH_3+3(COONa)_2$; and also by heating sodium formate with sodium phosphite or phosphate. M. E. Pozzi-Escott observed that phosphorus is hydrogenized by the hydrogenases—*e.g.* philothion.

The physical properties of phosphine.—At ordinary temp., phosphine is a colourless gas, which can be condensed to a colourless liquid, or frozen to a white solid. H. Rose[5] gave 1·146 for the **relative density** (air unity) ; J. B. A. Dumas, 1·1214 ; and H. Buff, 1·165. The theoretical value for PH_3 is near 1·175, and the lowered values are due to the presence of admixed hydrogen. G. Ter-Gazarian obtained for the purified gas the relative density 1·1829. The early determinations of the weight of a litre of gas are vitiated by the contamination of the phosphine with hydrogen ; G. Ter-Gazarian gave 1·5295 grms., and M. Bretschger, 1·5293 grms., for the **weight of a litre** of the gas under normal conditions. The literature was reviewed by M. S. Blanchard and S. F. Pickering. D. McIntosh and B. D. Steele gave 0·744 for the **specific gravity,** *D*, of the liquid at its b.p. $-86·2°$; and

	−107°	−101°	−97°	−91°	−87°	−81°	−79°
Sp. gr. . .	0·761	0·756	0·753	0·748	0·745	0·740	0·739

The **molecular volume** at the b.p. is 45·7 ; E. Rabinowitsch gave 47 for the mol. vol. R. Lorenz and W. Herz studied this subject. A. O. Rankine calculated $0·911 \times 10^{-15}$ sq. cm. for the mean collision area of phosphine. The sp. gr.,

D, at the temp., T° K., is $D=0{\cdot}744+0{\cdot}0005952(186{\cdot}8-T)$. D. McIntosh and B. D. Steele gave:

	−105·9°	−101·2°	−97·6°	−93·1°
Sp. gr. of liquid . .	0·760	0·756	0·753	0·746
Sp. gr. of vapour . .	0·00079	0·00101	0·00122	0·00151

S. Skinner gave for liquid phosphine:

	49·4°	44·4°	39·4°	29·4°	24·6°	18·4°	8·4°	2·4°
Press. .	62·4	56·1	50·8	41·3	37·1	32·6	27·2	23·4
Sp. gr. .	0·417	0·469	0·502	0·536	0·545	0·559	0·595	0·618

The **surface tension** of liquid phosphine was found by D. McIntosh and B. D. Steele to be:

	−105·9°	−101·2°	−97·6°	−93·1°
Surface tension, σ . . .	22·783	22·095	21·553	20·798 dynes per cm.
Mol. surface energy, $\sigma(MV)^{\frac{2}{3}}$.	287·2	279·6	273·4	265·4 ergs.

A. O. Rankine and C. J. Smith gave for the **viscosity** of phosphine gas 0·0001070 at 0°, 0·0001129 at 15°, and 0·0001450 at 100°; and for the constant C, 290. They calculated the area presented by the molecules for mutual collision to be $0{\cdot}911\times10^{-11}$ sq. cm. E. Briner measured the **compressibility** as represented by the relative values of pv at different temp. and press. He found:

24·6°	p .	1	10	15	20	25	30 atm.
	pv .	1	0·97	0·98	0·80	0·75	0·70
33·6°	p .	1	10	15	20	30	40 atm.
	pv .	1	0·94	0·89	0·85	0·77	0·62
46·2°	r .	1	30	35	40	45	50 atm.
	pv .	1	0·79	0·75	0·71	0·66	0·61
54·4°	p .	1	15	35	45	55	65 atm.
	pv .	1	0·92	0·80	0·72	0·61	0·47

According to M. Faraday, phosphine can be condensed to a transparent, colourless liquid by cooling it in a bath of carbon dioxide, when under a press. of 2–3 atm.; and K. Olschewsky cooled the gas to −75° by a mixture of solid carbon dioxide and ether, but no liquefaction occurred; at −90°, the gas condensed to a liquid which did not freeze at −110°. The gas can be readily liquefied in a tube cooled by liquid ethylene to −102·5, and it can then be frozen at −133·5° to a transparent, crystalline solid. S. Skinner found that the gas can be readily liquefied at ordinary temp. when under 30 atm. press. K. Olschewsky gave −85° for the **boiling point**; F. Henning and A. Stock, −87·43° at 760 mm.; and D. McIntosh and B. D. Steele, −86·2°. K. Olschewsky gave −132·5° for the **melting point.** D. McIntosh and B. D. Steele found the **vapour pressure** of the liquid to be:

	−105·9°	−101·2°	−97·7°	−93·1°	−86·6°
Vap. press.	237	319	393	498	719 mm.

F. Henning and A. Stock found rather smaller values, $\log p=-845{\cdot}57T^{-1}+1{\cdot}75\log T-0{\cdot}0061931T+4{\cdot}61480$. E. Briner gave 38·5 atm. at 25°; 46·5 atm. at 35°; 57 atm. at 45°; and 64·5 atm. at 51·3°. A. Stock and co-workers gave data between −87° and −111°. The **heat of vaporization** is $17{\cdot}2\times10^{10}$ ergs. S. Skinner gave 54° for the **critical temperature,** and 70·5 atm. for the **critical pressure;** corresponding data by A. Leduc and P. Sacerdote are respectively 52·8° and 64 atm.; by E. Briner, and P. A. Guye, 51·3° and 64·5 atm. S. Skinner gave 4·6 for the **critical volume.** J. Ogier gave for the **heat of formation,** (P,3H) = −36·6 Cals.; and for gaseous phosphine, −11·6 Cals. M. Berthelot and P. Petit obtained a similar result; while R. de Forcrand gave $(P_{gas},3H)-9{\cdot}1$ Cals.; and P. Lemoult gave for yellow phosphorus, and gaseous phosphine, −5·8 Cals.; he also gave for the **heat of combustion,** 310 Cals. at constant vol., and 311·2 Cals. at constant press. D. H. Drummond calculated for the **free energy** of the reaction $\frac{3}{2}H_{2gas}+\frac{1}{4}P_{4gas}=PH_{3gas}$, $-16486{\cdot}5+3{\cdot}72T\log T+0{\cdot}0004T^2+0{\cdot}0_67T^3+2{\cdot}52T$, or

$-RT \log K$, where $K = p_{PH_3}/p_{H_2}^{\frac{3}{2}} p_{P_4}^{\frac{1}{4}}$. The free energy of the formation of phosphine from hydrogen and solid phosphorus at 25° is −3296·0 cals. The entropy change in the reaction calculated from the free energy equation is −27·72; so that the **entropy** of phosphine at 25° is 52·4 units. J. C. Thomlinson compared the heats of formation of the trihydrides of the nitrogen-antimony family of elements.

Phosphine is decomposed by **heat** into phosphorus and hydrogen. D. M. Kooij [6] measured the progress of the reaction $2nPH_3 = 2nP + 3nH_2$ from the change in the press. of the gas after different intervals of time. If p_0 denotes the original press. of the gas with a mols of PH_3 in unit vol.; and p the press. of the mixture when x mols of a have decomposed, since for every 2 vols. of phosphine which disappear, 3 vols. of hydrogen remain, when ax mols of phosphine have decomposed, $\frac{3}{2}ax$ mols of hydrogen remain. Hence $a - ax$ mols of phosphine and $\frac{3}{2}ax$ mols of hydrogen remain at the time t. Consequently, $p_0 = a$, and $p = (1-x)a + \frac{3}{2}ax$. If the reaction is unimolecular, $PH_3 = P + 3H$, and

$$\frac{dx}{dt} = k(a - ax)\,; \quad k = \frac{1}{t}\log\frac{a}{a-ax}\,; \quad k = \frac{1}{t}\log\frac{p_0}{3p_0 - 2p}$$

In one experiment, D. M. Kooij found that when $p_0 = 715{\cdot}21$:

t	7·83	24·17	41·25	63·17	89·67
p	730·13	759·45	786·61	819·96	856·50
k	0·00236	0·00237	0·00235	0·00238	0·00241
Percentage decomposition	4·17	12·37	19·97	29·29	39·23

The constancy of k is in close agreement with the assumption that the reaction is unimolecular; and not so closely with assumptions that the reaction is bi-, ter-, or quadri-molecular. This may mean that the slow reaction: $PH_3 = P + 3H$, is followed by the very rapid formation of molecules of hydrogen and phosphorus; or it may mean that the reaction actually proceeds only in the adsorbed film of gas on the surface of the containing vessel, and that the velocity of the reaction in the adsorbed system is proportional to the press. of the gas in the interior of the vessel. The effect of the nature of the surface of the containing vessel must therefore be of importance, and D. M. Kooij found that the velocity coefficient k in a new vessel was 0·0023, in an old vessel it was 0·0064. He also measured the effect of temp. on the velocity constant k, and found :

	310°	367°	440°	512°
k	0·00021	0·00067	0·0025	0·0081

and he represented his results by the equation $\log k = -3595T^{-1} + 2{\cdot}4884$. M. Trautz and D. S. Bhandarkar measured the velocity in a porcelain vessel between 845° and 956°—above 956° the velocity was too rapid for measurement. Above 945°, the reaction is uninfluenced by the walls of the containing vessel, and takes place in the body of the gas. The reaction is retarded by water vapour, and accelerated by copper. According to C. N. Hinshelwood and B. Topley, the rate of decomposition of phosphine in a quartz bulb is affected by some activating influence, which, after a time, decreased to a constant minimum. Similarly also with a porcelain container. The addition of powdered fused silica of approximately known surface area caused an increase of velocity corresponding with the increased surface, so that, up to at least 771°, the reaction is to a large extent localized on the walls of the containing vessel, and not in the body of the gas—it is hence called a *wall-reaction.* This does not agree with M. Trautz and D. S. Bhandarkar's results. The rate of the reaction observed by C. N. Hinshelwood and B. Topley is unimolecular over the press. range 37·5 to 707 mm. The heat of activation is approximately constant between 40,000 and 50,000 cals. when the value calculated for a gas-reaction is 86,719 cals. between 940° and 960°. There is no evidence that the wall-reaction becomes a gas-reaction at higher temp. The reaction was studied by S. Dushman, D. H. Drummond, and E. Yamazaki.

B. H. Wilsden studied the energy involved in the electronic shifts during the dissociation of phosphine.

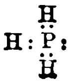
L. Bleekrode[7] gave 1·317 for the **index of refraction** of liquid phosphine at 17·5° for Na-light, and 1·323 at 11° for white light. P. L. Dulong gave for the gas at 0° for white light, 1·000789; and J. W. Brühl compared the results obtained with the μ- and the μ^2-formulæ.

The **spectrum** of the green flame of gases containing phosphine was found by P. Christofele and F. Beilstein, and G. Salet to have two intense green lines, one of which almost coincides with one of the green lines of barium. The spectrum of the burning gas is quite different from that furnished by free phosphorus; it can scarcely be attributed to the molecules PH_3 because at that temp., phosphine is dissociated into its elements. K. B. Hofmann attributes the spectrum to the chemical process in the inner mantle generating rays of a special refrangibility. J. N. Lockyer gave a photograph of the spectrum of phosphine. H. J. Emeléus found the spectrum of the flame of spontaneously inflammable phosphine burning in oxygen is the same as that of burning phosphorus (*q.v.*). J. E. Purvis observed no absorption bands in the ultra-violet.

H. Rose[8] said that spontaneously inflammable phosphine remains unaltered if confined over mercury or well-boiled water, and exposed to **light,** provided no vapour of phosphorus is present; and T. Graham made a similar observation with respect to the non-spontaneously inflammable gas. P. Thénard, however, showed that there is something wrong with H. Rose's experiment, for sunlight transforms the spontaneously inflammable gas into the other form, while the contained hydrogen hemi- and di-phosphides furnish an orange-red deposit, showing that some phosphine is decomposed. L. N. Vauquelin, U. J. J. Leverrier, and A. Vogel also found that the spontaneously inflammable gas gives a reddish deposit when exposed to sunlight. D. Amato, however, observed that dry but impure phosphine suffers no perceptible alteration when exposed to direct sunlight provided the temp. exceeds 10°. M. Trautz and D. S. Bhandarkar calculated the limit of photosensitiveness of phosphine to be about a wave-length of $329\mu\mu$. S. C. Roy studied the reaction from the point of view of the radiation hypothesis. Y. K. Sirkin found that the radiation theory fitted in with the decomposition of phosphine. R. Robl observed no fluorescence occurs with phosphorus in ultra-violet light.

J. Dalton,[9] H. Buff and A. W. Hofmann, and A. W. Hofmann found that phosphine is decomposed by the **electric discharge,** forming red phosphorus, and a vol. of hydrogen 1·5 times the original volume of the gas. T. Graham found that the electrification of the non-spontaneously inflammable gas converts it into the spontaneously inflammable gas. P. and A. Thénard said that the condensed electric discharge decomposes phosphine incompletely, for it first produces the hemiphosphide, then the diphosphide, and finally a red substance—red phosphorus. M. Berthelot also noted the formation of the diphosphide under these conditions, and he represented the reaction: $4PH_3=5H_2+P_4H_2$. B. Lepsius said that with the electric arc in phosphine, there is a dazzling red light, and the red clouds of phosphorus which are formed condense on the walls of the containing vessel as a mixture of red and yellow phosphorus.

The chemical properties of phosphine.—H. Davy[10] analyzed the gas, but his sample must have been mixed with so much hydrogen as to render his result useless for determining the composition of the gas. The analyses of H. Rose, J. B. A. Dumas, and U. J. J. Leverrier agree with the empirical formula PH_3; and the vapour density determinations previously indicated show that this is also the mol. formula. A. O. Rankine discussed the structure of the molecules of the family of trihydrides; H. Remy, and H. Henstock, the electronic structure; and G. W. F. Holroyd gave



$$\begin{array}{c}\mathrm{H}\\ \mathrm{H}:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{P}}}:\\ \mathrm{H}\end{array}$$

According to J. Meisenheimer and L. Lichtenstadt, when phosphine oxide, $O:PH_3$, has its hydrogen atoms replaced by three different radicles, the asymmetric compounds are optically active—*e.g.* $O:P(C_6H_5)(C_2H_5)(CH_3)$. P. Pascal also said that the magnetic properties are in agreement with the formula $O:PH_3$.

The gas has an odour suggesting a mixture of stinking fish and garlic; it is irrespirable. As shown by G. Maclean, it has no action on vegetable colours. The effects of heat, light, and the electric discharge have been indicated above. The gas has no perceptible effect on **hydrogen.** The gas does not support combustion, but when traces of hydrogen hemiphosphide are present, the gas may ignite spontaneously in **air** or in **oxygen**—Fig. 12; and H. Rose found that the inflammation occurs even if the temp. of the gas be near the f.p. of mercury, and the air at —15°. H. Davy gave 149° for the **ignition temperature** of the gas; P. Thénard, 100°; and A. W. Hofmann said that the ignition temp. of the purified gas exceeds 100°, because the gas can be bubbled through boiling water without the bubbles burning as they burst in air; on the other hand, the friction of the glass stopper of a glass vessel containing the gas may produce inflammation, K. Olschewsky found that the flame of the burning gas is not extinguished at —78°. but it is at —90°. H. Davy added that the inflammation of single bubbles of the gas is attended by a vivid light, and the formation of a thick, white, vortex ring of phosphoric acid; while in oxygen gas, the combustion is so brilliant as to resemble flashes of lightning. The products of combustion are phosphoric acid and water, as well as a little phosphorus pentoxide which is deposited as a film on the walls of the containing vessel. J. Dalton, and H. Buff found that the combustion of one vol. of the spontaneously inflammable gas consumes two vols. of oxygen. When a mixture with an excess of air or oxygen is exploded, one vol. of phosphine consumes two vols. of oxygen: $2PH_3+4O_2=3H_2O+P_2O_5$; but if self-accendible phosphine be bubbled into an excess of oxygen, some phosphorus is deposited as a yellowish-red film, and less oxygen is then consumed. To obtain complete combustion, J. B. A. Dumas recommended mixing the spontaneously inflammable gas with an equal vol. of carbon dioxide, and then with oxygen, but on igniting the mixture at 120°, he still found only 1·83 vols. of oxygen were consumed instead of two vols. H. Davy, and J. B. A. Dumas suggested that when less than 2 vols. of oxygen are consumed per vol. of phosphine, some phosphorus escapes combustion altogether, but H. Rose considered this to be improbable. H. Davy maintained that when the amount of oxygen associated with phosphine is insufficient for complete combustion, there is a preferential combustion of the phosphorus, and that free hydrogen remains unburnt. J. B. A. Dumas showed that the ignition by an electric spark of a mixture of one vol. of phosphine and 1½ vols. of oxygen contained in a narrow tube yields no phosphorus, but forms water and phosphorous acid, while the residual gas contains sometimes hydrogen, sometimes hydrogen and oxygen with some unoxidized phosphine. If a mixture of one vol. of phosphine with half a vol. of oxygen be exploded by rarefaction, phosphorus may be deposited, and the residual gas contains hydrogen and unconsumed phosphine.

A mixture of the non-accendible gas with oxygen does not ignite at ordinary temp. unless rarefied. According to J. J. Houton de la Billardière, if a glass tube surrounded by a wire-gauze be inclined over a mercury pneumatic trough, and partly filled with the mixture of oxygen and phosphine, an explosion immediately occurs if the gas-tube be raised into a vertical position so as to rarefy the gas a little; and, added J. B. A. Dumas, the explosion by alteration of level takes place with greater facility when an excess of phosphine is present. H. Rose found that a mixture of phosphine and air invariably explodes if kept at the ordinary press. over mercury for a few hours; and H. Davy showed that spontaneously inflammable phosphine can be mixed in a narrow glass tube—8 mm. diameter—without combustion owing to the cooling effect of the sides of the tube. T. Thomson showed that there is here a slow oxidation while phosphorous acid and hydrogen are formed.

The self-accendible gas loses its spontaneous inflammability when this slow oxidation is in progress a little while.

H. J. van de Stadt found that when phosphine and oxygen are mixed at low press., they rapidly combine with the emission of light, to form phosphorous acid: $2PH_3+3O_2=2H_3PO_3$. When the gases are brought in contact very slowly, there is an intermittent greenish-blue light, and equal vols. of oxygen and phosphine interact to form hydrogen and metaphosphorous acid which is deposited as a deliquescent, crystalline film on the walls of the containing vessel: $PH_3+O_2=H_2+HPO_2$. The slow oxidation of phosphine at greater press. proceeds nearly in accord with the equation $4PH_3+5O_2=2HPO_2+2H_3PO_3+2H_2$; does not increase the rate of oxidation continuously; but when a limiting low press. is attained an explosion suddenly occurs. Fig. 12 shows the rate of oxidation in press. decrease per hour, when the press. is expressed in millimetres of mercury at 50°. The limiting press. for explosion depends greatly on the amount of moisture present which retards or prevents oxidation. This is not a case opposing the need for the presence of moisture before certain chemical actions can take place. The effect of the superdrying of the reacting components has not been tried. P. Duhem considers that these experiments are analogous with those given for the oxidation of phosphorus in Fig. 12. H. J. Emeléus made a spectroscopic study of the light emitted by the low temp. combustion of phosphine.

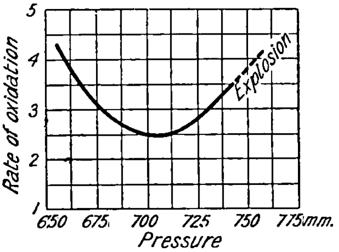


FIG. 12.—The Effect of Pressure on the Rate of Oxidation of Phosphine.

The solubility of phosphine in 100 vols. of **water** was found to be 1·8 vols. by P. Gengembre; 2·14 vols. by W. Henry; 2·5 vols. by H. Davy; 11·22 vols. by B. von Dybrowsky; 12·5 vols. by J. Dalton; and 25·0 vols. by J. M. Raymond. These deviations are great enough to render all the results of little value. A. Stock and co-workers found 100 vols. of water at 17° dissolve 26 vols. of phosphine. The aq. soln. of the gas smells like the gas itself, and, according to T. Thomson, tastes bitter. When the aq. soln. is boiled, the dissolved gas is expelled; the aq. soln. is not luminescent; when exposed to air, it gives off hydrogen gas, and forms phosphoric acid; and when it is exposed to light, red phosphorus is deposited. The aq. soln. does not react alkaline like the aq. soln. of ammonia. S. Skinner said that phosphine may be liquefied in contact with water, and it forms crystalline *hydrated phosphine.* No analyses of the crystals are available, but they are supposed to be *phosphonium hydroxide*, PH_3H_2O, *i.e.* PH_4OH—*vide infra.* They can be distilled from one part of the tube to another by gently warming them. L. Cailletet and L. Bordet found that the compressed gas condenses and floats on the surface of water present in the containing vessel, and a part dissolves. If the press. be suddenly released, a white crystalline product is formed which dissociates when the press. has reached 2·8 atm. at 2·2°; 3 atm. at 4°; 5·1 atm. at 9°; 9·8 atm. at 15°; and 15·1 atm. at 20°. The crystalline hydrate could not be formed above 28°.

In 1788, A. F. de Fourcroy and L. N. Vauquelin[11] said:

> Un petit morceau de phosphore attaché au bout d'un fil de fer, plongé dans le gaz acide muriatique oxygéné, s'allume en décrépitant, brûle rapidement et avec une véritable déflagration. Cette combustion a paru si rapide à M. Vauquelin, qui le premier l'a aperçue, et à M. de Fourcroy qu'ils ont pensé qu'elle pourrait être employée avec avantage pour faire l'acide phosphorique.

Phosphine takes fire in **chlorine** at ordinary temp. and press., burning with a brilliant greenish-white flame, and combining with four times its vol. of chlorine —T. Thomson said 3 vols. of chlorine; and H. Davy, 4 to 5. A. W. Hofmann obtained a similar result with phosphine of a high degree of purity. A. Stock found that phosphine and chlorine react at low temp. According to A. J. Balard, **bromine** decomposes the spontaneously inflammable gas, forming phosphorus and hydrogen bromide; and A. W. Hofmann observed that purified phosphine inflames on making contact with bromine water. T. Thomson found that when **iodine** is introduced into the spontaneously inflammable gas, phosphorus and hydrogen iodides are formed; and A. W. Hofmann observed that with the dried gas and a suitable temp., phosphonium iodide is produced, $5I_2+8PH_3=2PI_2+6PH_4I$—*vide infra.* J. Ogier found that when a mixture of equal vols. of phosphine and **hydrogen chloride** is compressed to 20 atm. at 14°, phosphonium chloride is formed; and the union occurs at lower press. by cooling—thus, the combination occurs at ordinary press., and —30° to —35°. S. Skinner mixed 3·7 vols. of liquid hydrogen chloride, and 4·6 vols. of liquid phosphine—near its critical temp.—and obtained approximately half the vol. of phosphonium iodide —*vide infra.* Phosphine also unites with dry **hydrogen bromide** to form phosphonium bromide; and, as shown by J. J. Houton de la Billardière, with dry **hydrogen iodide** to form phosphonium iodide—*vide infra.* A. J. Balard found that **chlorine monoxide** detonates in contact with phosphine; and **hypochlorous acid** forms phosphoric and hydrochloric acids—J. Dalton obtained a similar result with **calcium hypochlorite.** L. Moser and A. Brukl represented the reaction with soln. of **iodic acid** by $8HIO_3+5PH_3=5H_3PO_4+4I_2+4H_2O$.

As shown by H. Davy, F. Jones, etc., when **sulphur** is heated in phosphine gas, phosphorus sulphide and hydrogen sulphide are formed—one vol. of phosphine furnishing 1·5 vols. of hydrogen sulphide—T. Thomson, L. N. Vauquelin, J. B. A. Dumas, and H. Davy did not obtain the theoretical proportion of hydrogen sulphide, but, without a doubt, they used impure phosphine. F. Jones said that phosphine is decomposed by sulphur more slowly than is the case with arsine or stibine. L. Delachaux observed that if phosphine be heated with more sulphur than is needed to convert all the hydrogen into hydrogen sulphide, the reaction can be symbolized: $2PH_3+nS=3H_2S+P_2S_{n-3}$, and above 450°, the ratio of the press., p, to the absolute temp., T, is constant, showing that the reaction is complete. With relatively smaller proportions of sulphur, this ratio continues to increase for some time, even at 500°, and the gaseous phase consists of a mixture of hydrogen sulphide and phosphine, and the solid phase of phosphorus, which is gradually covered with phosphorus sulphide formed by interaction between the constituents of the gas phase. The reaction between **hydrogen sulphide** and phosphine does not occur with any appreciable velocity below 320°, and above this temp. the ratio p/T increases continuously with the time, no equilibrium being reached. The products are hydrogen and a variable mixture of phosphorus sulphides. A. W. Hofmann found that triethyl phosphine readily reacts with sulphur, forming the sulphide, $(C_2H_5)_3PS$, but it has no action on hydrogen sulphide. J. Dalton, and A. J. Balard found that **sulphur dioxide,** and **sulphurous acid** react at ordinary temp. with phosphine, forming water and phosphorus sulphide. A. Cavazzi represented the reaction between phosphine and sulphurous acid at 60°–70° by the three equations: (i) $PH_3+H_2SO_3=H_3PO_2+H_2O+S$; (ii) $2H_3PO_2+H_2SO_3=2H_3PO_3+H_2O+S$; and (iii) $2H_3PO_3+H_2SO_3=2H_3PO_4+H_2O+S$; and in the presence of mercury the reaction progresses: $PH_3+H_2SO_3+Hg=H_3PO_2+H_2O+HgS$. H. Rose found that when phosphine is passed over dried **sulphur trioxide,** at ordinary temp., red phosphorus and sulphur dioxide are formed; G. Aimé's observations indicate that a yellow cloud of sulphur is produced, and a blue liquid appears in the vessel next day—the blue liquid was thought to be a soln. of sulphur in sulphur trioxide—A. J. Balard reported the formation of both sulphur and phosphorus, as well as of sulphur dioxide. A. Stock and co-workers found that 100 vols. of 50 per cent. **sulphuric acid** dissolve 5 vols. of phosphine at 17°; and H. Buff said that cold conc. sulphuric acid absorbs phosphine without chemical action, but if heated, phosphine acts as a powerful reducing agent on sulphuric acid. A. J. Balard also said that with conc. sulphuric acid, sulphur, phosphorus, and hydrogen sulphide are produced ; and H. Rose, sulphur, phosphoric acid, and sulphur dioxide. The reaction was studied by T. Humpert. W. R. Hodgkinson added that the gas is at first rapidly absorbed by the conc. acid without any visible change, but when the acid is saturated, and the passage of the gas is continued, the acid rapidly becomes hot enough to ignite the gas. If the acid be kept cool, while an excess of gas is passed into it, it is reduced to sulphur dioxide with the separation of sulphur: $3H_2SO_4+2PH_3=2SO_2+S+2H_3PO_4+3H_2$; if hydrogen sulphide is produced, it is at once decomposed by the sulphur dioxide. If the gas be passed for a sufficient length of time, while the acid is kept cool, it becomes so thick and viscid with the separated sulphur, that the containing vessel may be inverted without the contents escaping. At low temp., A. Besson found that sulphuric acid furnishes a syrupy liquid which forms a white deliquescent solid, supposed to be *phosphonium sulphate—vide infra.* H. W. F. Wackenroder said that **pentathionic acid** is not decomposed by phosphine. A. Besson reported that **sulphuryl chloride** reacts with phosphine in the cold. precipitating a brownish-red mixture of phosphorus trisulphide and phosphorus, and hydrogen chloride ; the liquid contains phosphoryl chloride, phosphorous acid, and some undecomposed sulphuryl chloride. Phosphine was also found to react with **thionyl chloride**, forming a reddish precipitate consisting of phosphorus and phosphorus trisulphide; the liquid separates into two layers. The upper one contains thionyl chloride, and phosphoryl and thiophosphoryl chloride. No definite compound was obtained from the residue left on distilling the upper layer in vacuo at 200° ; nor could any definite compound be isolated from the lower layer. R. Böttger observed that when phosphine is passed into a soln. of a **tellurium salt**, tellurium phosphide is precipitated.

For the action of **nitrogen** on phosphorus, *vide* phosphorus nitride. According to T. Graham,[12] the gas which is not spontaneously inflammable becomes so if it be admixed with a trace of the vapour of **nitrous acid** or **nitrogen trioxide**—one vol. of this compound in 10,000 of the non-spontaneously inflammable gas can make it accendible ; a drop of nitric acid on the mercury confining the phosphine will produce enough gas to effect the transformation ; sulphuric acid fresh from the lead chambers contains enough nitrous anhydride so to convert phosphine bubbled through the acid ; hydrogen prepared from zinc and sulphuric acid fresh from the lead chambers when mixed with phosphine makes it spontaneously inflammable. Washed nitric oxide does not transform phosphine, but the unwashed nitric oxide may do so. Phosphine rapidly attacks fuming **nitric acid**, but an acid of sp. gr. 1·34 is not attacked. H. H. Landolt, and A. W. Hofmann made purified phosphine spontaneously inflammable in air by bubbling the gas through nitric acid containing a trace of nitrous anhydride. A. Besson found that phosphine can reduce conc. nitric acid so as to impart the necessary amount of nitrous anhydride to make it spontaneously inflammable provided the temp. exceeds —25°. T. Graham found that anything which destroys the nitrous anhydride makes the spontaneously inflammable gas non-accendible. J. Dalton found that phosphine at ordinary temp. reduces **nitric oxide** to nitrous oxide in a few hours ; and a mixture of nitric oxide and phosphine can be detonated by an electric spark to form nitrogen, water, and phosphoric acid ; P. Thénard found that **nitrous oxide** and phosphine—say in the vol. proportions of 3 : 1—can be detonated by the electric spark, to form, according to T. Thomson, 3 vols. of nitrogen, phosphoric acid, and water. J. B. A. Dumas said that 21 vols. of nitrous oxide are needed for 4 vols. of phosphine. The equation can be written: $2PH_3+8N_2O=P_2O_5+3H_2O+8N_2$. T. Graham said that phosphine is scarcely affected by **nitrogen peroxide**.

According to T. E. Thorpe and A. E. H. Tutton, **phosphorous oxide** has no action on phosphine either cold or hot. H. Rose, and R. Mahn found **phosphorus trichloride** reacts with phosphine, forming hydrogen chloride and phosphorus, but A. Besson said that at ordinary temp. hydrogen diphosphide, not phosphorus, is formed. A. Stock said that the reaction does not occur, notably at —20°, while it does occur slowly with **phosphorus tribromide** at —20°. P. de Wilde also said that the reaction with the tribromide is faster than with the trichloride. J. H. Gladstone represented the reaction $PBr_3+PH_3=2P+3HBr$, but this will be wrong if A. Besson is right. R. Mahn symbolized the reaction with **phosphorus pentachloride**: $3PCl_5+PH_3=4PCl_3+3HCl$, and, as H. N. Stokes pointed out, this is not analogous with the reaction with ammonium chloride, $PCl_5+NH_4Cl=4HCl+PNCl_2$, which corresponds with $PCl_5+NH_3=3HCl+PNCl_2$. J. H. Gladstone represented the reaction with **phosphorus pentabromide,** $3PBr_5+PH_3=4PBr_3+3HBr$. T. Graham found that arsenic acid is decomposed by phosphine, forming arsenic and water; and A. Cavazzi found that a soln. of **arsenic trioxide** in hydrochloric acid acts on phosphine, forming arsenic phosphide. A. Besson observed that phosphine does not form a complex with the **arsenic halides** —fluoride, chloride, bromide, or iodide—but there is a vigorous reaction with the evolution of the hydrogen halide and the formation of a brown solid which, by elutriation, can be separated into two substances with compositions $PAsO_3$ and $PAsO_6$. H. Buff found that when **antimony** is heated in the gas, antimony phosphide is formed, and 1·5 vols. of hydrogen per vol. of phosphine. R. Böttger observed no precipitation when phosphine is passed into soln. of **antimony salts,** nor did P. Kulisch obtain any precipitation with soln. of potassium antimonite, or of tartar emetic. H. Rose said that an addition product is formed by the action of phosphine on **antimony pentachloride,** but R. Mahn could obtain no complex salt, and represented the reaction: $4SbCl_5+PH_3=4SbCl_3+PCl_5+3HCl$. R. Böttger obtained no precipitate by passing phosphine into soln. of **bismuth salts**; on the contrary, P. Kulisch found that bismuth phosphide is deposited. A. Cavazzi said that phosphine at 100° forms with **bismuth trichloride** what is probably black bismuth phosphide; a black precipitate—$Bi_5Cl_2P_4$—is produced when phosphine acts on an aq. dil. soln. of bismuth trichloride; and with a hydrochloric acid soln., there is no precipitate. A. Cavazzi and D. Tiroli found that phosphine acts on an ethereal soln. of **bismuth tribromide,** forming a black hygroscopic substance with the composition Bi_3Br_7P.

J. Hunter[13] found that one vol. of fresh cocoanut **charcoal** absorbs at ordinary temp. 69·1 vols. of phosphine—reduced to n.p. θ; and one vol. of campechy wood charcoal, 27·5 vols. of phosphine. T. Graham's observations on this subject are indicated above. A. Frank studied the action of phosphine on the **metal carbides.** M. Berthelot passed a mixture of **carbon dioxide** and phosphine through a hot glass tube, but could not establish the formation of either methane or of any hydrocarbons, C_nH_n. L. Cailletet and L. Bordet compressed a mixture of equal vols. of phosphine and carbon dioxide in the presence of water, and obtained a white crystalline mass which decomposed at 22°—it was thought to be a *hydrated carbon phosphinodioxide;* or possibly a complex of phosphonium hydroxide and octohydrated carbon dioxide. By treating a mixture of **carbon disulphide,** water, and phosphine in a similar way, they obtained a *hydrated carbon phosphinodisulphide.* A. W. Hofmann found that phosphine is not acted on by carbon disulphide at ordinary temp., but triethylphosphine reacts violently with carbon disulphide producing $(C_2H_5)_3P.CS_2$; while it has no action on **mercaptan.** H. Davy said that phosphine is soluble in alcohol, ether, and volatile oils. J. Messinger and C. Engels found that phosphine does not act on **aldehyde** unless a hydrogen halide is present. C. Schultz-Sellac found a yellow substance, not zinc phosphide, is formed when phosphine acts on an ethereal soln. of **zinc ethide.** A. W. Hofmann obtained triethyl phosphine by the action of phosphine on ethyl iodide under press. Like ammonia, phosphine forms a series of **alkyl phosphines** analogous with the amines; these compounds are less basic than the ammonia derivatives. The tertiary phosphines were discovered by P. Thénard in 1846, and A. W. Hofmann established the existence of the primary and secondary products in 1871. Phosphine, and the primary aliphatic phosphines are weak bases, and form salts unstable in water; the introduction of alkyl groups strengthens them so that the secondary phosphines are decomposed only by alkalies. The tertiary phosphines react like well-defined bases. The aromatic phosphines are less basic than the amines, and are all decomposed by water. P. and A. Thénard obtained a substituted phosphine by the action of **ethylene** on phosphine. J. de Girard obtained a compound of phosphine and **chloral hydrate.** A. Hoffman showed that when phosphine is passed into a warm soln. of **formaldehyde** acidified with hydrochloric acid, *tetramethylphosphonium chloride*, $P(CH_3)_4Cl$, of m.p. 151°, is formed. G. Cauquil found that **cyclo-hexanol** dissolves 2856 c.c. of phosphine per litre at 25° and 766 mm. B. von Dybkowsky found that **blood** takes up more phosphine than water; for putting the solubility of phosphine in water at 0·1122 at 15°, the value for arterial blood is 0·2673, and for venous blood 0·13.

A. Besson found that phosphine does not act on **boron trifluoride** at ordinary temp., but at −30°, or better at −50°, a complex is formed—**boron hemiphosphinotrifluoride,** $2BF_3.PH_3$; below 20°, **boron trichloride** forms **boron phosphinotrichloride,** $BCl_3.PH_3$; and at ordinary temp., **boron tribromide** forms **boron phosphinotribromide,** $BBr_3.PH_3$. At ordinary temp., **silicon tetrafluoride** does not react with phosphine; at −50°, much gas is absorbed, but no crystals are formed even at −60°; if, however, the mixture be compressed at 20 atm. and 10°, crystals of presumably a **silicon phosphinotetrachloride** which decompose at 15 atm., are formed. An analogous **silicon phosphinotetrabromide** appears to be formed by the action of phosphine on **silicon tetrabromide.** H. Rose reported the formation of a **titanium phosphinotetrachloride** by union with **titanium tetrachloride.** J. Gewecke discussed the action of phosphine on silicon and titanium tetrachlorides, and also on zirconium and thorium tetrachlorides—*vide* the corresponding phosphides.

J. L. Gay Lussac and L. J. Thénard [14] showed that **potassium** or **sodium** decompose phosphine *promptement*, when it is heated in the gas, forming metal phosphide, and, according to H. Davy, and J. Dalton, liberating about 1·5 vols. of hydrogen per vol. of phosphine employed—when allowance is made for the impure nature of the gas they must have used. H. Buff, and J. B. A. Dumas obtained a similar result with **copper**; H. Buff with **zinc**; and J. B. A. Dumas with **iron.** E. Rubenovitch found that with copper the reaction begins at 180°–200°—*vide* the metal phosphides. Compounds formally analogous with the amides by replacing one hydrogen atom in the phosphine molecule with an alkali metal have been prepared by A. Joannis. Thus, **sodiophosphine,** with the empirical formula, $NaPH_2$—called by A. Joannis *phosphidure de sodium*—is obtained by treating a soln. of sodium in liquid ammonia with phosphine. Towards the end of the reaction the compound in question floats on the surface of the liquid as brownish-red globules of fluid which freeze to a solid when slowly cooled. When the solid is heated to about 65°, the excess of ammonia is expelled and sodiophosphine remains as a white solid. **Potassiophosphine,** KPH_2, is obtained in slender needle-like crystals in a similar manner. If these compounds be heated, they form the corresponding phosphide: $3KPH_2=2PH_3+PK_3$; they are also decomposed by water with the evolution of phosphine. When treated with nitrous oxide, the alkali phosphines yield a vol. of nitrogen equal to the vol. of nitrous oxide employed.

B. Franke represented action of **potassium hydroxide** in dil. soln. by the equation: $4PH_3+4KOH=4PH_2OK+4H_2$; and $4PH_2OK=P_4H_2+H_2+4KOH$, *vide infra*, the alkali phosphides. I. Guareschi found that spontaneously inflammable phosphine loses this quality if passed over **soda-lime.** According to P. Kulisch, phosphine exerts no perceptible chemical action on **potassium or sodium chloride** or **sodium carbonate**—hot or cold; the same remark applies to **calcium and barium chlorides**; but A. Winkler showed that aq. soln. of the salts of the alkalies, alkaline earths, on the earthy metals, furnish the corresponding phosphites or hypophosphites. P. Kulisch found that soln. of the lighter metal salts are not affected by phosphine hot or cold, but with soln. of salts of the heavy metals, either the salt is reduced to the metal, or a metal phosphide is formed; in some cases both the metal and the phosphide are produced. The reduction probably proceeds in stages; with cupric sulphate, for instance, cuprous sulphate is probably formed: $8CuSO_4+PH_3+4H_2O \rightarrow H_3PO_4+4H_2SO_4+4Cu_2SO_4$; and by the further action of phosphine, cuprous phosphide: $3Cu_2SO_4+2PH_3 \rightarrow 3H_2SO_4+2Cu_3P$, and free copper: $4Cu_2SO_4+PH_3+4H_2O \rightarrow H_3PO_4+4H_2SO_4+8Cu$, are formed. M. Bretschger examined soln. of cupric sulphate, and of cuprous chloride as absorbents of phosphine in gas analysis. H. Rose added that with some halides, a phosphide is formed and hydrogen halide is set free, in other cases, phosphonium salts analogous to those of ammonium are formed. J. M. Raymond, T. Thomson, and H. Rose found that **copper salts** are decomposed by phosphine, but, according to R. Böttger, this is not so. H. Rose said that phosphine decomposes soln. of cupric chloride; P. Kulisch, that the cupric chloride is reduced to cuprous chloride; and E. Rubenovitch, that there is no reaction. The last-named added that the action proceeds in a different way with the different salts of copper—aq. soln. of cupric sulphate give a phosphide, $Cu_5P_2.H_2O$; soln. of cupric formate and acetate give an oxygenated phosphide, Cu_2PO; and ammoniacal soln. of copper salts in the absence of air yield copper tritaphosphide. L. Moser and A. Brukl found that a copper sulphate soln. is a slower absorbent for phosphine than soln. of mercuric, silver, or gold salts. The reaction is symbolized: $3CuSO_4+PH_3+3H_2O=H_3PO_3+3Cu+3H_2SO_4$; $4CuSO_4+PH_3+4H_2O=H_3PO_4+4Cu+4H_2SO_4$; and $3CuSO_4+2PH_3=Cu_3P_2+3H_2SO_4$, accompanied by $Cu_3P_2+3Cu=2Cu_3P$. Red **cuprous oxide** is rapidly blackened by phosphine, forming the tritaphosphide. J. Riban found that phosphine is rapidly absorbed by hydrochloric acid soln. of phosphine, forming **cuprous phosphinochloride,** $CuCl.PH_3$, or $Cu_2Cl_2.2PH_3$, and, according to P. Kulisch, some phosphide is formed at the same time. The copper phosphinochlorides were also studied by M. Bretschger. J. M. Raymond, T. Thomson, H. Rose, P. Kulisch, and R. Böttger found that aq. soln. of **silver salts** are decomposed by phosphine, and, according to R. Böttger, dry silver nitrate is likewise decomposed. According to T. Poleck and K. Thümmel, when filter-paper moistened with a drop of silver nitrate soln. is exposed to phosphine the wet spot is coloured egg-yellow and the periphery acquires a dark brown ring which slowly broadens towards the centre until the whole spot becomes black as in the analogous case of arsine. The yellow spot is not changed by nitric acid, but when wetted with water or aq. ammonia it is immediately blackened. If phosphine be passed into a conc. soln. of silver nitrate, the first few bubbles give a deep lemon-yellow coloration, and the liquid acquires an acid reaction—no precipitate is formed. The coloration remains for one or two days, and then becomes colourless—silver is precipitated, and the soln. contains phosphorous and phosphoric acids. If a rapid stream of phosphine be passed into a conc. soln. of silver nitrate at 0°, the whole liquid solidifies to a yellow crystalline mass which rapidly blackens owing to the separation of silver. The yellow precipitate is considered to be **silver trinitratophosphide,** $Ag_3P.3AgNO_3$. It is best to dilute the phosphine with carbon dioxide or hydrogen since otherwise each bubble of gas in the conc. soln. of silver nitrate produces a flash of light. D. Vitali said that an explosion sometimes occurs. With a dil. soln. of silver nitrate, the black precipitate is formed at once, and the soln. contains a mixture of nitric, nitrous, phosphoric, and hypophosphorous acids. The action is represented $PH_3+6AgNO_3=Ag_3P.3AgNO_3+3HNO_3$, followed by $Ag_3P.3AgNO_3+3H_2O=6Ag+3HNO_3+H_3PO_3$. L. Moser and A. Brukl represented the reaction with an excess of silver nitrate: $3AgNO_3+PH_3=PAg_3+3HNO_3$; and $PAg_3+AgNO_3+2H_2O=H_3PO_2+4Ag+HNO_3$, as well as $H_3PO_2+2AgNO_3+H_2O=H_3PO_3+2Ag+2HNO_3$ and $H_3PO_3+2AgNO_3+H_2O=H_3PO_4+2Ag+2HNO_3$. The resultant reaction is therefore represented: $8AgNO_3+PH_3+4H_2O=H_3PO_4+8Ag+8HNO_3$. J. M. Raymond, H. Rose, R. Böttger, P. Kulisch, and T. Thomson found that aq. soln. of **gold salts** are reduced to gold or gold phosphide by phosphine; but R. Böttger said that dry gold chloride is not affected by the gas. A. Cavazzi represented the action with a dry ethereal soln. of gold chloride by: $AuCl_3+PH_3=AuP+3HCl$. The reaction with 0·2N-$AuCl_3$ is represented by L. Moser and A. Brukl by $2AuCl_3+PH_3+3H_2O=2Au+H_3PO_3+6HCl$; $4AuCl_3+PH_3+4H_2O=H_3PO_4+4AuCl+8HCl$; $3AuCl+PH_3=Au_3P+3HCl$; $3Au_3P+AuCl_3+6H_2O=10Au+3H_3PO_2+3HCl$; $3H_3PO_2+2AuCl_3+3H_2O=2Au+3H_3PO_3+6HCl$; and $3H_3PO_3+2AuCl_3+3H_2O=2Au+3H_3PO_4+6HCl$. The resultant reaction is therefore represented $8AuCl_3+3PH_3+12H_2O=8Au+24HCl+3H_3PO_4$.

J. M. Raymond, T. Thomson, A. Brukl, and R. Böttger found that soln. of **zinc or cadmium salts** are not affected chemically by phosphine, but soln. of **mercury salts** are decomposed. H. Rose said that mercuric sulphate and nitrate give white precipitates which are compounds of mercury phosphide with the metal salt, with mercuric chloride, the yellow precipitate is a mixture of mercurous chloride and mercury phosphide. J. B. A. Dumas heated dry mercuric chloride in phosphine and obtained three vols. of hydrogen chloride per vol. of phosphine, and a yellowish-red powder. W. R. Hodgkinson found that an alcoholic soln. of mercuric cyanide forms a precipitate which is extremely sensitive to light, and which contains mercury cyanide and phosphide. The reactions were also studied by T. Thomson, D. Vitali, and A. Brukl. L. Moser and A. Brukl represented the reaction with soln. of mercuric chloride: $6HgCl_2+2PH_3=3HgCl_2.P_2Hg_3+6HCl$; $6HgCl_2+PH_3+3H_2O=H_3PO_3+6HCl+6HgCl$; and $8HgCl_2+PH_3+4H_2O=H_3PO_4+8HCl+8HgCl_2$. P. Lemoult said that mercuric chloride and bromide form respectively **mercury chlorophosphide,** Hg_3Cl_3P, and **mercury bromophosphide,** $Hg_5Br_4P_2$; and that both salts can be used as absorbents for phosphine in analytical work. Similarly with mercuric iodide which forms **mercury iodophosphide,** Hg_3I_3P. K. A. Aschan obtained three chlorophosphides, $3Hg_3P_2.7HgCl_2$, by the action of phosphine on an aq. soln. of mercury chloride. The first is yellow, $3Hg_3P_2.7HgCl_2$—H. Rose reported $2PHg_2Cl.HgCl_2.3H_2O$; second, red, $4Hg_3P_2.5HgCl_2$; and third, brown, $Hg_3P_2.HgCl_2$. According to H. Rose, the reaction between phosphine and mercuric nitrate furnishes the complex **mercury nitratophosphide,** $P_2Hg_3\{Hg(NO_3)_2HgO\}_2$, where the mercury is all bivalent. This explosive substance was examined by K. A. Aschan; and S. Hada believes that it is a mercurous salt related to his mercurous nitratohypophosphite. T. Graham found that phosphine slowly decomposes dry **mercurous oxide,** but not **mercuric oxide**; and P. Kulisch found that **thallous oxide** is reduced to thallium. R. Böttger observed no precipitate is produced by the action of phosphine on soln. of **tin salts.** H. Rose obtained a yellow addition product with a tin tetrachloride, but R. Mahm represented the reaction: $3SnCl_4+2PH_3=Sn_3Cl_6P_2+6HCl$. J. M. Raymond, A. Brukl, and T. Thomson observed that soln. of **lead salts** are decomposed by phosphine, but R. Böttger said that no precipitate is formed, while H. Rose said that the precipitation occurs very slowly. The results with arsenic, antimony, and bismuth salts are indicated above. W. P. Winter observed that phosphine reduces a soln. of **ammonium molybdate** to a blue soln. which becomes colourless when warmed or allowed to stand. H. Rose found that **chromic chloride** is decomposed by phosphine with the liberation of much heat. J. M. Raymond, and T. Thomson observed no reaction when phosphine is passed into soln. of **manganese salts.** F. Jones represented the reaction with potassium permanganate: $6KMnO_4+4PH_3=3Mn_2O_3+2K_2HPO_3+2KH_2PO_3+3H_2O$, in agreement with the effect of ammonia, arsine, and stibine on this liquid. A. Cavazzi represented the reaction: $2KMnO_4+PH_3=K_2HPO_3+H_2O+2MnO_2$, and by $2KMnO_4+PH_3=K_2HPO_4+H_2O+Mn_2O_3$. J. M. Raymond, T. Thomson, and R. Böttger observed no precipitation occurs when phosphine is passed into soln. of **iron salts,** though H. Rose said that ferric chloride is decomposed, or, according to P. Kulisch, reduced to ferrous chloride. R. Böttger said that soln. of **cobalt and nickel salts** are not decomposed by phosphine; H. Rose said that the chlorides are decomposed. R. Schenck found that nickel phosphide is formed when phosphine is passed into a soln. of nickel chloride containing enough tartaric acid to prevent the precipitation of nickel hydroxide by alkali-lye. R. Böttger said that soln. of **platinum, rhodium, and iridium salts** are not precipitated by phosphine, but H. Rose said these soln. are rapidly decomposed. According to R. Böttger, soln. of **palladium salts** give a precipitate of the phosphide; but phosphine does not react with dry palladium monoxide. A. Cavazzi represented the reaction with a neutral aq. soln. of platinum atetrchloride: $PtCl_4+2PH_3=PtCl_2+2HCl+P_2H_4$; and $PtCl_2+P_2H_4=PtP_2H_2+2HCl$.

The physiological action of phosphine.—Experiments on pigeons, rats, and other animals, and a few observations on men show that phosphine has an exciting action on the respiratory mucous membranes, and a secondary action on the nervous system. It is possible that the phosphine acts on the oxyhæmoglobin, forming phosphorous acid. The spectrum of the blood of animals poisoned by phosphine has an absorption band in the violet. The subject has been investigated by J. Clark and T. B. Henderson,[15] J. Brilliant, M. Koschlakoff and H. Popoff, B. von Dybkowsky, etc. Cases of phosphine poisoning have been reported on board ships laden with ferrosilicon containing phosphides as impurities; when moistened by rain, the phosphide gives off phosphine which penetrates into the cabins, and when respired by sailors, etc., has caused a number of deaths—*vide* ferrosilicon, 6. 40, 13. According to M. Jokote, one part of phosphine in 100,000 parts of air is poisonous in 16 to 30 hrs.; air with 2·5 in 100,000 is poisonous in 8·5 to 10 hrs.; and air with 1 : 10,000 proved fatal in 2·5 to 3·5 hrs. M. Brenner thus described a pharmaceutist who is supposed to have been for a long time in an atmosphere contaminated with a minute proportion of phosphine:

> The man was engaged for two and a half years in the preparation of hypophosphites; his illness commenced with spots before the eyes, and inability to fix the attention. His teeth became very brittle, and pieces broke from healthy as well as diseased teeth from very slight causes. Finally, a weakness of the arms and limbs developed in the course of nine months into complete locomotor ataxy.

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§ 10. The Phosphonium Compounds

When phosphine is brought in contact with hydrogen chloride, bromide, or iodide under suitable conditions, a series of phosphonium compounds are formed in which the PH_4-radicle plays the same part as the ammonium radicle in the ammonium compounds. The possible existence of **phosphonium-amalgam,** analogous to ammonium amalgam, was indicated by A. Besson,[1] who electrolyzed a soln. of the so-called phosphonium sulphate in sulphuric acid, at —25° to —40°, by means of a platinum anode and a mercury cathode. Bubbles of gas were developed in the mercury, showing that if phosphonium forms an amalgam with mercury, it is very unstable even at that low temp. The possible formation of an unstable **phosphonium hydroxide,** PH_4OH, analogous with ammonium hydroxide, NH_4OH, was indicated in connection with the experiments of L. Cailletet and L. Bordet, and of S. Skinner on the action of press. on water and phosphine. Of the three halides which have been prepared, the iodide is relatively stable, the chloride is very unstable.

According to H. Rose,[2] hydrogen chloride and non-accendible phosphine do not react perceptibly on one another even in sunlight, and borax or water absorbs the hydrogen chloride from the mixture, but if the mixture be passed through aq. ammonia, the unabsorbed gas acquires the property of inflaming spontaneously in air. A. Bineau suggested that this circumstance favours the assumption that the gases combine without condensation to form **phosphonium chloride,** PH_4Cl, just as phosphine and hydrogen bromide or iodide unite without condensation, but the compound with hydrogen chloride does not liquefy at —12°. J. Ogier found that when equal vols. of the mixed gases are compressed by 20 atm. press. at 14°, union occurs and crystals of the salt are formed ; if lower press. are used, the temp. must be reduced to the temp. of liquid sulphur dioxide. G. Lemoine found 2 atm.

press. was sufficient to make the gases unite; and, according to S. Skinner, the temp. and press. required for the combinations are:

	−30°	7°	13°	18°	21°	24°	28·5°	45°
Press. .	1	11·6	19·3	27·3	33·6	39·1	47·2	85·3 atm.

J. H. van't Hoff compared the phenomenon of dissociation with that of evaporation. He compressed a mixture of equal vols. of phosphine and hydrogen chloride until the tube was half filled with phosphonium chloride crystals. The tube was now heated by means of a water-bath. Fusion occurred at 25°, and at 50°–51° and a press. of 80–90 atm., the line of demarcation between liquid and gas disappeared; whilst on cooling, the thick clouding which characterizes the critical point was observed. F. E. C. Scheffer represented the press.-temp. relations, more or less diagrammatically by Fig. 13. *G* represents the m.p. curve of phosphonium chloride; the plait-point represents *H*, the critical temp. of that salt; *AC*, the vap. press. curve of hydrogen chloride; *BD*, the vap. press. curve of phosphine; and *GI*, the sublimation curve of phosphonium chloride. The double curve *GH* represents the boiling and dew curves, Fig. 7, of **1.** 4, 8. E. Briner gave for the compressibility, represented by the relative values of pv:

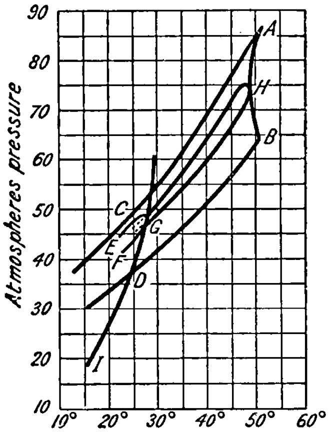

FIG. 13.—Pressure-Temperature Relations of Mixtures of Phosphine and Hydrogen Chloride.

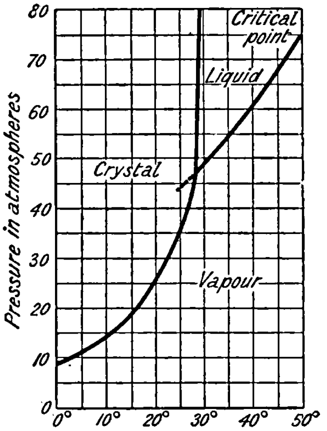

FIG. 14.—Vapour Pressures of Phosphonium Chloride.

33·5°	p	1	40	45	50 atm.
	pv	1	0·69	0·65	0·58
54·4°	p	1	45	60	80 atm.
	pv	1	0·72	0·61	0·38

These values fall between those for hydrogen chloride and phosphine. He also gave for the vap. press. of phosphonium chloride:

	25°	30°	35°	40°	45°	50°
Vap. press. . .	38·5	42·5	46·5	51·5	57	63

and these values fall between the corresponding values for the component gases—hydrogen chloride and phosphine. The white crystals of phosphonium chloride were found by S. Skinner to melt at 26°; and he gave 48° for the critical temp., 96 atm. for the critical press., and 3·5 for the critical vol. G. Tammann gave for the critical temp. and press. respectively 48·8°–50·1° and 74·2–75·0 atm. His values for the vap. press. are shown in Fig. 14. F. M. G. Johnson's estimate of the dissociation press. of phosphonium chloride is indicated in Fig. 13. E. Briner found the critical temp. to be 49·1°; the critical press., 72·7 atm.; the heat of formation of a mol of gas 16·4 Cals.; the temp. at which the dissociation press. is one atm., 253°; and the number of mols produced by the dissociation of a mol of phosphonium chloride, 2. He also gave the heat of formation, $HCl_{gas}+PH_{3gas}=PH_4Cl_{solid}+43{\cdot}4$ Cals., hence the heat of sublimation is 43·4–16·4=27·0 Cals. per mol.

G. S. Sérullas[3] made **phosphonium bromide,** PH_4Br, in 1831 by mixing equal volumes of phosphine and bromine; by bringing a vessel containing a little silicon tetrachloride and water under a globe filled with phosphine; and by the action of phosphonium iodide on mercuric bromide. Hydrogen bromide and phosphine do not interact at ordinary temp., but A. Besson showed that a reaction occurs if dry phosphine be passed into a soln. of hydrogen bromide in phosphoryl chloride or other indifferent solvents. J. Ogier obtained it by passing a stream of phosphine through a cold conc. soln. of hydrogen bromide, filtering off the precipitate, drying by press., etc., and subliming the product in a sealed tube. A. Damoiseau prepared it by heating a mixture of yellow phosphorus and hydrogen bromide in a sealed tube between 100° and 120°. According to A. Richardson, some phosphonium bromide is formed when a mixture of hydrogen bromide and moist red phosphorus is exposed to sunlight: $2P+3H_2O+HBr=PH_4Br+H_3PO_3$. Phosphonium bromide is a mass of white or colourless cubic crystals which, according to A. Bineau, sublime at about 30°. The vap. density given by A. Bineau is 1·906 in agreement with the dissociated mol PH_3+HBr. The value required for PH_4Br is 1·987. The compound readily dissociates: $PH_4Br\rightleftharpoons HBr+PH_3$. F. Isambert studied the reaction at different temp., and found the results to be in accord with the law of mass action, both for phosphonium bromide alone, and when an excess of either component is present. If p_1 and p_2 denote the partial press. of the respective components ammonia and phosphine, and p the dissociation press. of phosphonium bromide, then, for equilibrium, $p_1p_2=\frac{1}{4}p$. The following is a selection from F. M. G. Johnson's measurements of the dissociation press:

	−80°	−36°	−14·2°	0°	14·4°	23·0°	38·8°
Pressure .	1	4	17	56	159	291	794 mm.

or the dissociation press. is one atm. at 38°. A demonstration experiment was devised by G. S. Newth. J. H. van't Hoff compared the phenomenon of the dissociation of the solid with the phenomenon of evaporation, but he did not obtain anything analogous to the critical state as was observed with phosphonium chloride. J. Ogier found the heat of formation to be $PH_{3gas}+HBr_{gas}=PH_4Br_{solid}+23{\cdot}03$ Cals.; $Br_{liquid}+4H+P_{solid}=PH_4Br+44{\cdot}1$ Cals. Phosphonium bromide is closely analogous with the corresponding iodide. G. S. Sérullas showed that it may inflame spontaneously in air, and is very deliquescent; it decomposes in contact with water, forming phosphine and hydrogen bromide: $PH_4BrAq.=PH_{3gas}+HBrAq.-3{\cdot}03$ Cals. A. Besson found that phosphonium bromide does not react with phosphoryl chloride at ordinary temp., but in a sealed tube at 50°, the reaction, $POCl_3+PH_4Br=3HCl+HBr+P_2O$, occurs; there is also a slow reaction with carbonyl chloride at 0°, but at 50°, in a sealed tube, the reaction, $6PH_4Br+5COCl_2=10HCl+6HBr+5CO+2PH_3+P_4H_2$, proceeds vigorously.

The best-known member of the series of phosphonium halides is **phosphonium iodide,** PH_4I. It was discovered by J. J. Houton de la Billardière[4] in 1817, who found that when dried phosphine and hydrogen iodide are mixed together, colourless crystals are formed. It is true that about four years earlier J. L. Gay Lussac obtained a white sublimate consisting of cubic crystals by the action of iodine on phosphorus in the presence of a little water, but he paid no further attention to the product; G. S. Sérullas showed that in the reaction, $2P+I_2+4H_2O=H_3PO_4+HI+PH_4I$, which occurs when the mixture of iodine, phosphorus, and a little water is heated in a retort, the hydrogen iodide is first evolved, and the phosphonium iodide then sublimes. H. Rose found that a mixture of phosphorus, iodine, with a little hydroiodic acid gave rather better results than G. S. Sérullas' mixture. A. Oppenheim heated a mixture of red phosphorus and conc. hydriodic acid in a sealed tube at 160° and obtained a sublimate of crystals of phosphonium iodide. A. Damoiseau passed hydrogen iodide over heated phosphorus: $2P+HI+3H_2O=PH_4I+H_3PO_3$; and A. Richardson exposed moist red phosphorus to the action of hydrogen iodide in sunlight, and observed that phosphonium iodide is probably formed. A. Holt and J. E. Myers, and A. von Bäyer evaporated the solvent from a soln. of 100 grms. of phosphorus and 175 grms. of iodine in carbon disulphide in a current of carbon dioxide; he then gradually added 50 grms. of water, and obtained approximately 120 grms. of a thick crust of a sublimate of phosphonium iodide resembling ammonium chloride : $(4P+I_2)+7H_2O=2PH_4I+H_3PO_3+H_3PO_4$. A. W. Hofmann also made it by the action of water on phosphorus triiodide or a mixture of phosphorus and iodine :

Place 100 grms. of phosphorus in a retort, *A*, and add an equal weight of carbon disulphide, and then 170 grms. of pure iodine. Keep the retort well cooled during the mixing. Distil off the carbon disulphide by attaching a condenser to the retort, and placing the retort in a dish of warm water. The retort is then connected with a wide tube, *B*, which may be fitted with a glass bottle, *R*, as shown in Fig. 15, and then, in the fume closet, with a wash-bottle containing water to absorb any hydrogen iodide formed by the decomposition of the phosphonium iodide. Connect the retort with an apparatus, *C*, for generating carbon dioxide, dried by passage through a tube, *D*, charged with pumice-stone soaked with sulphuric acid, and keep a slow stream of carbon dioxide passing through the apparatus all the time an experiment is in progress. Let 85 grms. of water fall slowly, drop by drop, on to the residue in the retort. The heat of the reaction suffices to sublime the phosphonium iodide into the wide tube, but towards the end of the operation, the retort may be warmed. When the operation is completed, loosen the phosphonium iodide which has collected in the wide tube by means of a piece of wire, and transfer the salt to the bottle used as a receiver. The bottle is then closed with its stopper, *S*. The reaction is represented : $5I_2+18P+32H_2O=10PH_4I+8H_3PO_4$.

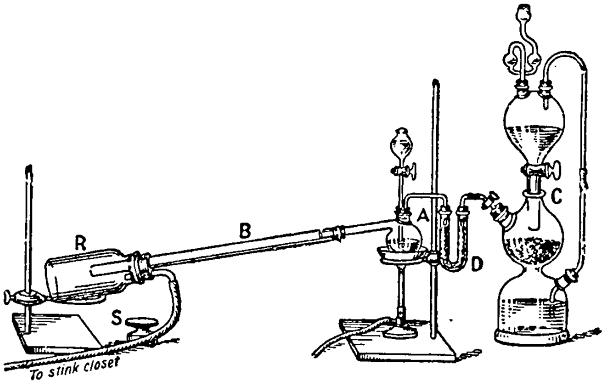

FIG. 15.—The Preparation of Phosphonium Iodide.

A. W. Hofmann made phosphonium iodide by the action of phosphine, dried by quicklime, on iodine: $8PH_3+5I_2=P_2I_4+6PH_4I$. A. L. Ponndorf obtained phosphonium iodide by the action of hydrogen iodide on hypophosphorous acid : $3H_3PO_2+HI=2H_3PO_3+PH_4I$; and K. Lissenko, by saturating molten hypophosphorous acid with hydrogen iodide and cooling the mass while in the presence of the gas. On warming the product in an atm. of carbon dioxide, phosphonium iodide, iodine, and hydrogen iodide were given off, while phosphoric acid remained. J. J. Houton de la Billardière thought that spontaneously inflammable phosphine and the non-accendible form furnished different varieties of phosphonium iodide, but H. Rose, and U. J. J. Leverrier showed that the products are identical.

The analyses of H. Rose agree with the formula just assigned to phosphonium iodide, namely, PH_4I. According to J. L. Gay Lussac, and J. J. Houton de la Billarbière, the clear, transparent crystals are cubic, while H. Rose described them as square prisms with terminal edges and truncated angles. L. Wagner found the crystals, though cube-like in appearance, really belong to the tetragonal system, and the axial ratio for methyl phosphonium iodide is $a:c=1:0{\cdot}7310$. R. G. Dickinson gave for phosphonium iodide $1:0{\cdot}729$, and he found the X-radiograms in agreement with a unit-cell of the dimensions $6{\cdot}34\times6{\cdot}34\times4{\cdot}62$ A. He showed that the space-lattice of the low temp. form of ammonium chloride is very similar to that for phosphonium iodide if the halogen atoms of the former are a little displaced. The arrangement of the atoms is indicated in Fig. 16, and that for low temp. form of ammonium chloride in Fig. 17. The black circles represent phosphorus or nitrogen atoms, and the circles halogen atoms. The hydrogen atoms may be grouped about the phosphorus tetrahedrally, but not necessarily so that all the atoms are equivalent. In the diagrams *OA*, *OA*, and *OC* are the axes of the unit. L. Wagner gave 2·860 for the sp. gr. of phosphonium iodide; H. Rose said that the crystals can be sublimed backwards and forwards in a sealed tube without melting. A. Bineau gave 80° for the sublimation temp. H. Rose said that the crystals deposit phosphorus and acquire a yellow tinge when they are gently heated, but G. S. Sérullas found that the vapour can be passed without decomposition through a red-hot tube containing fused borax. A. Smith and R. P. Calvert found the dissociation press. of solid phosphonium iodide to be :

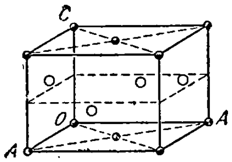

FIG. 16.—Space-lattice of Phosphonium Iodide.

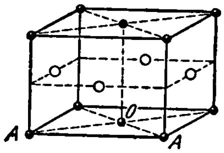

FIG. 17.—Space-lattice of the Ammonium Chloride.

	15°	30°	40°	50°	60°	62·6°	66°
Pressure .	36	107·8	199	368·1	660	760	917·3

The results are in agreement with those of F. M. G. Johnson, which are illustrated by Fig. 18, where the dissociation press. of one atm. is at 62°. A. Holt and J. E. Myers have concluded that, in carefully dried phosphonium iodide vapour, there occurs a secondary reaction in which the hydrogen iodide and phosphine give some free hydrogen and phosphorus iodide. Such a change was indicated in the experiments of A. Smith and R. P. Calvert by a slow, uniform increase in the press. with the time. A. Holt and J. E. Myers state that phosphorus iodide is not formed if a trace of moisture is present. For this reason, perhaps, F. M. G. Johnson obtained no evidence of its formation. According to J. Ogier, the heat of formation is $PH_{3gas}+HI_{gas}=PH_4I_{solid}+24{\cdot}17$ Cals.; and $P_{solid}+I_{solid}+4H=PH_4I_{solid}+29{\cdot}5$ Cals. J. J. Houton de la Billardière found that the salt is not decomposed by **oxygen.** H. Rose said that the crystals fume in **air,** and they gradually deliquesce in moist air giving off phosphine; and H. Rose, and J. J. Houton de la Billardière found that the salt is hydrolyzed by **water** and aq. soln. of ammonia or alkali hydroxide giving off phosphine—*vide supra,* preparation of phosphine. J. Ogier gave for the heat of decomposition $PH_4I+Aq.=PH_{3gas}+HIAq.+4{\cdot}77$ Cals.

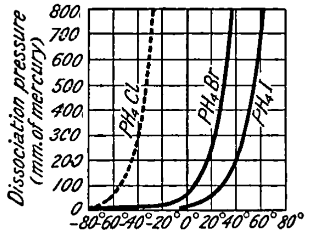

FIG. 18.—Dissociation Pressures of the Phosphonium Halides.

Phosphonium iodide is a reducing agent, which A. W. Hofmann considered to produce more satisfactory results in many cases than hydrogen iodide. It is also used in the preparation of organic phosphines. According to J. C. Cain, **chlorine** and water convert phosphonium iodide into a mixture of red phosphorus and hydrogen diphosphide. A. Stock saw that at —100° phosphonium chloride and chlorine react to form phosphorus pentachloride if chlorine be in excess; and with phosphine in excess, the reaction is slower, and on gradually warming the mess to room temp., yellow hydrogen diphosphide is formed which changes to reddish hemienneaphosphide, or red phosphorus. Hydrogen hemiphosphide is formed from the intermediate product, $PH_2Cl+PH_3=P_2H_4+HCl$, as in the case of ammonia. R. Hanslian found phosphonium iodide is decomposed by **iodine,** forming phosphorus and hydrogen iodides. J. J. Houton de la Billardière said the salt is not decomposed by **hydrochloric acid** ; and G. S. Sérullas found that the salt at ordinary temp. is inflamed by **chloric, bromic or iodic acid,** while **perchloric acid** acts only slowly even when warmed. The dry **chlorates, bromates, and iodates** also inflame phosphonium iodide at ordinary temp.; **potassium perchlorate** decomposes it slowly even when warmed. J. J. Houton de la Billardière found that **hydrogen sulphide** is without action on the salt; while G. S. Sérullas showed that **sulphuric acid** is reduced by phosphonium iodide, forming hydrogen sulphide and sulphur dioxide, which react so that the result of the reaction is to produce sulphur, phosphorus, iodine, a phosphorous acid, and hydrogen iodide. H. Rose, J. J. Houton de la Billardière, A. W. Hofmann, C. F. Rammelsberg, and J. Messinger and C. Engels found that with a conc. soln. of **ammonia,** phosphine is given off and ammonium iodide is formed. G. S. Sérullas found that with **nitric acid** at ordinary temp., phosphonium iodide bursts into flame; while dry **potassium nitrate** decomposes it only slowly even when warmed. According to E. and P. Fireman, **phosphorus pentachloride** acts but slowly at ordinary temp., and only at the points of contact: $3PCl_5+3PH_4I=PI_3+PCl_3+12HCl+4P$. P. de Wilde observed that much heat is developed by the action of **phosphorus trichloride** on phosphonium iodide, forming hydrogen chloride, phosphine, hydrogen diphosphide, phosphorus tetraiodide, etc. A. Besson found that **phosphoryl chloride** reacts vigorously at about 100°, forming hydrogen chloride, phosphorus tetraiodide, red phosphorus, and metaphosphoryl chloride; while when heated with **thiophosphoryl chloride,** there was no sign of the formation of phosphorus thiodiiodide, P_2SI_2. E. and P. Fireman represented the action of **antimony pentachloride** at 100°–110° in a sealed tube, by the equation: $3SbCl_5+3PH_4I=SbI_3+2SbCl_3+9HCl+PH_3+2P$; at ordinary temp. the reaction proceeds with explosive violence. J. J. Houton de la Billardière, and H. Jahn found that **carbon dioxide** has no action on phosphonium iodide. G. S. Sérullas said that it is decomposed by **alcohol,** forming ethyl iodide and phosphine. G. S. Sérullas showed that the iodide is not decomposed by hot **acetic acid.** J. de Girard examined the action of phosphonium iodide on **aldehyde ;** and S. Litthauer, on **benzaldehyde.** E. Drechsel said that phosphonium iodide does not react with **carbon disulphide** below 140°, but above that temp. trimethyl-phosphonium iodide is formed: $3CS_2+4PH_4I=P(CH_3)_3HI+CH_2S+3PSI$. H. Jahn observed a number of other products—phosphine, methane, and traces of other hydrocarbons, hydrogen sulphide, and a dark red substance with the composition $C_5H_6S_7P_6O_{12}$. A. Besson represented the reaction with **carbonyl chloride :** $4PH_4I+8COCl_2=16HCl+8CO+P_2I_4+2P$; and J. Traube found that it does not react with moist **cyanogen chloride.** According to G. S. Sérullas, **mercuric cyanide,** or **potassium cyanide,** reacts with phosphonium iodide, forming mercuric or potassium iodide, hydrogen cyanide, and phosphine.

J. J. Houton de la Billardière found phosphonium iodide has no action on **mercury.** G. S. Sérullas showed that dry **silver nitrate** reacts vigorously with phosphonium iodide with the development of much heat, forming silver iodide and phosphate; **silver oxide** forms silver iodide and spontaneously inflammable phosphine; **mercurous chloride** gives mercuric iodide, hydrogen chloride, and phosphine; and **mercurous bromide** forms mercuric iodide, and phosphonium bromide. E. and P. Fireman represented the reaction with **tin tetrachloride** at about 100° in a sealed tube: $4SnCl_4+4PH_4I=SnI_4+3SnCl_2+10HCl+2PH_3+2P$; and at 250° to 260°, $6SnCl_4+6PH_4I=3SnCl_2+3SnI_2+18HCl+2PH_3+4P$.

H. Rose,[5] H. Buff, A. Stock and co-workers, A. J. Balard, and W. R. Hodgkinson made observations on the action of phosphine on sulphuric acid. According to A. Besson, when hydrogen phosphide is passed into sulphuric acid at the ordinary temp., there is considerable development of heat, sulphur separates, and sulphurous acid is formed. If the acid is previously cooled by means of ice and salt, the gas is somewhat largely absorbed, and the liquid remains limpid. After a time, however, it begins to decompose in the manner indicated, the temp. rises, and decomposition becomes very rapid. If the acid is cooled to —20° or —25° by the rapid evaporation of methyl chloride, a syrupy liquid is obtained, from which a white, crystalline, highly deliquescent solid separates; this seems to be **phosphonium sulphate.** When thrown into water at the ordinary temp., it dissolves with a strident noise, and hydrogen phosphide is evolved, but the sulphuric acid is not reduced. When exposed to air at the ordinary temp., the phosphorus is oxidized to phosphoric, phosphorous and hypophosphorous acids, whilst the sulphuric acid is reduced to sulphurous acid and sulphur, with a small quantity of hydrogen sulphide. For the electrolysis of the soln., *vide supra*, phosphonium-amalgam.

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§ 11. The Lower Hydrogen Phosphides

The history of these phosphides has been reviewed in connection with phosphine. The so-called *liquid hydrogen phosphide*, or **hydrogen hemiphosphide,** P_2H_4, was obtained by P. Thénard[1] in 1845 by passing the gases obtained by the action of water on calcium phosphide, Ca_3P_2, through a U-tube immersed in a freezing mixture. Ten years earlier, U. J. J. Leverrier had suggested that some hydrogen phosphide other than phosphine was contained in spontaneously inflammable phosphuretted hydrogen. The first action of water on the calcium phosphide is supposed to result in the formation of this compound: $Ca_3P_2+6H_2O=3Ca(OH)_2+P_2H_4+H_2$; and much of the hydrogen hemiphosphide so formed is at the same time decomposed into hydrogen diphosphide and phosphine: $5P_2H_4=6PH_3+P_4H_2$. A. W. Hofmann prepared the gas by this process; and L. Gattermann and W. Hausknecht recommended the following modification:

A 3-necked Woulfe's bottle, *A*, about 3 litres capacity, is fitted up as shown in Fig. 19 One tube, *H*, is for the introduction of hydrogen; a second tube (about 2·5 cms. bore) serves for the introduction of the calcium phosphide. Both these tubes dip beneath the surface of the 1·5 litres of water contained in the bottle. A third tube for the exit gases is fitted with a vertical condenser, *B*, so that most of the moisture may be removed from the gas. The liquid hydrogen phosphide condenses in a suitable tube, *C*, cooled by a freezing mixture. The gas then passes to a second Woulfe's bottle, *D*, containing conc. hydrochloric acid in which any liquid phosphide in the gas is converted into a yellow solid; the gas passes on and is ignited in the flue. After the air has been expelled from the apparatus by the current of hydrogen, and the large Woulfe's bottle heated to about 60° by means of a water-bath, fragments of calcium phosphide about the size of a pea are introduced at the rate of about 50 grms. in 15–20 minutes. When about a quarter of this amount has been added, liquid phosphide begins to collect in the condenser. A yield of between 3 and 4 c.c. of liquid is obtained for every 100 grms. of calcium phosphide.

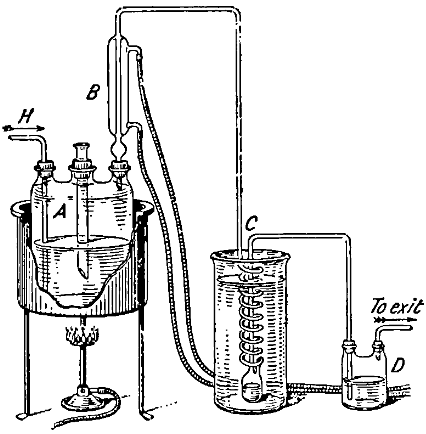

FIG. 19.—The Preparation of Liquid Hydrogen Phosphide.

A. Michaelis and M. Pitsch said that this same phosphide is formed when acetyl chloride reacts with hypophosphorous acid, in a side reaction involving: $4H_3PO_2=H_3PO_4+H_3PO_3+H_2O+P_2H_4$.

Hydrogen hemiphosphide at ordinary temp. is a colourless, strongly refracting liquid which, according to L. Gattermann and W. Hausknecht, has a sp. gr. 1·007 at 16°, and 1·016 at 12°; and a vap. density 74·73 to 77·0 in agreement with the value 76 required for the formula P_2H_4—formally analogous with hydrazine, N_2H_4; and if the phosphorus be here tervalent, the graphic formula is probably $H_2=P-P-H_2$. M. Croullebois also found the vap. density in agreement with this formula, which is based on the analyses of L. Gattermann and W. Hausknecht, and P. Thénard. No reliance can be placed on the vapour density determinations because the vapour is probably the decomposition products of the hemiphosphide. P. Thénard said that the liquid does not solidify at —20°, and it vaporizes between 30° and 40°, and at the same time is more or less decomposed. L. Gattermann and W. Hausknecht gave 57° to 58° for the b.p. at 735 mm. press. No residue remains provided the temp. does not exceed 80°. The distilled liquid is even less stable than the original. Sealed tubes containing the liquid should not be kept for any length of time since, owing to decomposition: $5P_2H_4=6PH_3+P_4H_2$, the internal press. may reach the bursting point. No deposition of any solid occurs when the liquid is kept for some time, but the liquid becomes yellow, presumably owing to the solubility of the solid diphosphide in the liquid hemiphosphide. P. Thénard found that the liquid decomposes when exposed to light, forming about 38 per cent. of the solid diphosphide, and 62 per cent. of phosphine: $5P_2H_4=6PH_3+P_4H_2$. This is in agreement with the observations of L. Gattermann and W. Hausknecht.

P. Thénard said that the liquid is spontaneously inflammable in air, and the presence of a trace of the vapour—1 : 500—makes phosphine and other combustible gases spontaneously inflammable in air. The white flame furnishes a thick white smoke of phosphorous oxide. V. Merz and W. Weith, and A. W. Hofmann found that a mixture of red and yellow phosphorus is deposited on a piece of cold procelain held in the flame of the burning hemiphosphide. P. Thénard found the liquid hemiphosphide to be insoluble in water; while alcohol, and turpentine appear to dissolve the liquid, but the soln. is very unstable, and rapidly decomposes. As in the case of hydrogen dioxide, the liquid hemiphosphide decomposes in contact with different substances which act as catalysts; for instance, an indefinitely large quantity is decomposed by a c.c. of hydrogen chloride gas, or, according to A. Stock and co-workers, by charcoal, pumice-stone, wadding, etc. L. Gattermann and W. Hausknecht tried unsuccessfully to prepare compounds of the liquid hemiphosphide with aldehydes and ketones similar to those formed by hydrazine.

H. Rose[2] observed a yellow powder is formed during the decomposition of potassium phosphide by water, and G. Magnus showed that when this substance is heated, it gives off hydrogen, and he therefore called it *Wasserstoffphosphor.* P. Thénard showed that the yellow solid has the empirical composition of **hydrogen diphosphide,** P_2H, and this is in agreement with analyses by R. Schenck, and L. Amat. Mol. wt. determinations agree with the formula, $(P_2H)_6$, or $P_{12}H_6$. This compound is often referred to as *yellow or solid hydrogen phosphide.* U. J. J. Leverrier found that when phosphine is exposed to light, yellow flakes of the solid hydrogen phosphide are produced; and P. Thénard obtained a greenish-yellow residue in the preparation of phosphuretted hydrogen from alkali-lye and phosphorus, and this he regarded as an isomeric modification of the yellow solid phosphide. H. Rose, P. Thénard, and R. Schenck also observed the formation of the diphosphide in the action of water on calcium phosphide; and P. Jolibois in the action of conc. hydrochloric acid on zinc phosphide. The usual method of preparation is by the action of water on calcium phosphide. This process was employed by A. Stock and co-workers, H. Rose, M. Croullebois, R. Schenck, and P. Thénard. W. Lenger's directions are as follow :

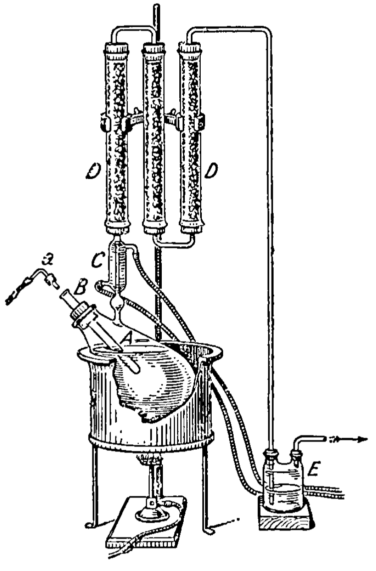

FIG. 20.—W. Lenger's Apparatus for the Preparation of Solid Hydrogen Phosphide.

A 3-litre flask, Fig. 20, three-fourths filled with water, is fitted up as shown in the diagram, and placed in a water-bath at 60°. A tube (2 cms. bore), *B*, is fitted into the neck of the flask by a rubber stopper; this tube dips below the surface of the water in the flask and serves for the introduction of the calcium phosphide. The gases first pass through a vertical condenser, *C* (about 10 cms. long), in order to remove most of the moisture, and then through three tubes (45 cms. long, and 2·5 cms. bore), *DD*, filled with fragments of calcium chloride about the size of a pea. About 200 or 250 grms. are needed to charge the tubes. The calcium chloride used should dissolve in dil. hydrochloric acid without residue. The calcium chloride tubes are protected from light by covering them with black paper. The liquid hydrogen hemiphosphide accompanying the phosphuretted hydrogen is decomposed on coming in contact with the calcium chloride. The exit tube dips below the surface of conc. hydrochloric acid in a 2-necked bottle, *E*, before it leaves the system; if the calcium chloride tube be not working properly, some flakes of yellow hydrogen diphosphide will appear in the acid. The escaping gas is thence led to the flue, and there ignited. When the calcium phosphide has been all added (about a kilogram in 6 hrs.), a stream of carbon dioxide is sent through the system by connecting *a* with the tube dipping in the flask. Most of the yellow hydrogen diphosphide will be found in the first two calcium chloride tubes, and it can be recovered by dissolving the contents in dil. hydrochloric acid (about 500 c.c.) cooled to 0°, and well stirred to prevent local heating. The solid diphosphide, floating on the surface of the acid, is washed with ice-cold water for about 5 minutes, then washed with alcohol, and finally with ether which has been distilled from sodium; and the solid is then allowed to stand for about 12 hrs. over concentrated sulphuric acid in vacuo. The yellow diphosphide must be protected from light during these operations. A kilogram of calcium phosphide furnishes from 6 to 8 grms. of the yellow hydrogen diphosphide. The dry product is best preserved in an ice-chest, since at ordinary temp. it is liable to decompose and turn a red colour.

P. Thénard showed that the solid diphosphide is formed by the action on the hemiphosphide (*q.v.*) of light, hydrochloric acid, volatile chlorides, and many other substances; and it is likewise formed under similar conditions from spontaneously inflammable phosphine which contains some hemiphosphide. D. Amato observed its formation by the partial oxidation of spontaneously inflammable phosphine at 10°–12°: $5P_2H_4+9O_2=6H_3PO_3+P_4H_2$. M. Berthelot noticed the formation of the diphosphide when phosphine is exposed to the electrical discharge: $4PH_3=5H_2+P_4H_2$; and U. J. J. Leverrier, when chlorine mixed with an equal vol. of carbon dioxide is passed into an excess of phosphine; with chlorine alone, the temp. produced is so high that phosphorus separates alone. P. de Wilde, and A. Besson observed the formation of the solid diphosphide by the action of phosphorus trichloride or tribromide on phosphine. A. Stock and co-workers added that the yields are small. A. Besson obtained the solid hydride by the action of phosphine on silicon hexachloride at —10°. F. Rüdorff showed that the solid diphosphide is formed when phosphorus diiodide is treated with water: $10P_2I_4+45H_2O=2PH_3+3H_3PO_4+11H_3PO_3+40HI+2(P_2H)$—W. Hittorf said that red phosphorus is the product of this reaction: $3PI_2+3H_2O=6HI+P_2O_3+P$. A. Stock and co-workers said the reaction is not suited for preparing the solid diphosphide. P. de Wilde noticed that the solid diphosphide is formed along with phosphine, etc., when phosphorus trichloride acts on phosphonium iodide; and J. C. Cain found it among the products of the action of chlorine on phosphonium iodide. A. Joly obtained the yellow diphosphide among the products of the action of metaphosphoric acid on phosphorous acid at 120°; and L. Amat, by heating a mixture of phosphorous acid and phosphorus trioxide. A. Colson observed the formation of the solid diphosphide when a soln. of phosphorus in turpentine is heated to 250°.

Hydrogen diphosphide, prepared by P. Thénard, U. J. J. Leverrier, and R. Schenck, is described as a canary-yellow powder without smell or taste. According to A. Stock and co-workers, the sp. gr. of the solid is 1·83 at 19°; J. Ogier found the heat of formation from yellow phosphorus to be $(4P,H_2)=35·4$ Cals. The mol. wt. determined by R. Schenck and E. Buck from the lowering of the f.p. when dissolved in molten phosphorus is 376, in agreement with 379 calculated for $P_{12}H_6$. A. Stock and co-workers found that the diphosphide can be preserved in darkness over a desiccating agent for 24 hrs. without appreciable change, but when exposed to air, it acquires an acid reaction, and gives off phosphine. They also showed that it is quickly decomposed when exposed to light; and U. J. J. Leverrier reported that when submerged in water hydrogen is evolved, and phosphoric acid is formed. According to U. J. J. Leverrier, the diphosphide decomposes into its elements when heated to 175° in a current of carbon dioxide, and in air it ignites between 140° and 150° according to its state of subdivision. It also decomposes when heated in an atm. of hydrogen, forming phosphine, and with a stronger heating, phosphorus. L. Amat said that when slowly heated to 215°, it decomposes as represented by the equation: $P_{12}H_6=2PH_3+10P$; and R. Schenck observed a slight decomposition when heated in vacuo at 100°. A. Stock and co-workers said that in vacuo gas begins to come off, and the decomposition almost ceases at 200°, but begins again at 260°, indicates the possible existence of another solid phosphide—*vide infra*. The diphosphide is inflamed when suddenly heated to 100°, or when struck with a hammer. U. J. J. Leverrier found the diphosphide is insoluble in water and alcohol; and, added P. Thénard, it is not dissolved in any liquid, other than the hemiphosphide, without decomposition. R. Schenck and E. Buck showed that it is soluble in molten phosphorus, forming a yellow liquid. A. Stock and co-workers found it is not soluble in liquid phosphine, nor in any liquid tried other than molten phosphorus, and hydrogen hemiphosphide. P. Thénard showed that the diphosphide decomposed by chlorine or chlorine-water, forming hydrogen chloride and phosphorus pentachloride in the former case, phosphoric acid in the latter case. P. Thénard found that when mixed with potassium chlorate it detonates when struck with a hammer, or when warmed a little; the diphosphide is rapidly decomposed by sulphuric acid, the acids of chlorine, and nitric acid; and, added U. J. J. Leverrier, a drop of conc. nitric acid causes inflammation, while with dil. nitric acid, it is decomposed and dissolved. R. Schenck showed that the diphosphide is blackened when treated with conc. aq. ammonia. A. Stock and co-workers, and W. Lenger found that the diphosphide dissolves in liquid ammonia at —40°, evolving phosphine and forming a red liquid, resembling $\frac{1}{20}N$-iodine soln., but in a few days becomes pale yellowish-red. When the sealed tube is opened, and the ammonia and phosphine have escaped, there remains a black solid—hydrogen enneaphosphide associated with ammonia. When the diphosphide is treated with piperidine, an energetic reaction occurs, phosphine is evolved, and there is produced hypophosphorous acid and a black solid—**hydrogen amminodiphosphide,** $P_{12}H_6.3NH_3$—which R. Schenck believes is to be regarded as **ammonium hydrotetraphosphide,** NH_4P_4H, where P_4H_2 is considered to be a monobasic acid. P. Thénard found that phosphorus pentachloride acts on the diphosphide like chlorine, but phosphorus trichloride, stannous chloride, or titanium tetrachloride has no action. A mixture of the diphosphide with silver oxide or mercuric oxide detonates feebly by percussion; and a mixture with cupric oxide detonates vigorously when heated. An alcoholic soln. of potassium hydroxide decomposes the diphosphide, giving off hydrogen and phosphine, and forming a red soln. which with water gives a yellow precipitate, and some hypophosphite is formed at the same time. The precipitate was thought by U. J. J. Leverrier to be a suboxide, and by A. Michaelis and M. Pitsch to be a tetritoxide: $P_4H_2+H_2O=P_4O+2H_2$, or, according to B. Francke, $P_4H_2+KOH=P_4HOK+H_2$, from which acetic acid precipitates solid $P_4H.OH$. U. J. J. Leverrier said that copper and silver salts are decomposed by the diphosphide; and a soln. of copper sulphate gives a black precipitate of copper, and copper phosphide.

B. Francke said that phosphorus hemiiodide is prepared by mixing the required quantities of phosphorus and iodine in carbon disulphide soln., and gradually adding the soln. to water with constant agitation. No separation of phosphorus occurs, but the aq. soln. of *phosphorus hydrohydroxyhydroiodide,* $OH.P_4H,HI$, becomes a golden-yellow colour, whilst the carbon bisulphide becomes colourless. The aq. layer is separated and heated to 80°, when it becomes colourless, deposits yellow flocks, and contains now only hydriodic and a little hypophosphorous acids. The yellow flocks are said to be *phosphorus hydrohydroxide,* $P_4H.OH$. This substance decomposes, slowly under water, more rapidly in moist air, into hypophosphorous acid, phosphorus, and gaseous hydrogen phosphide. When strongly heated in a current of carbon dioxide, the residue consists of phosphorus and phosphorus pentoxide. A. Michaelis and M. Pitsch, and K. Weidner consider these products to be the impure tetritoxide.

According to A. Stock and co-workers, and W. Lenger, indications of the formation of a solid hydrogen phosphide different from the yellow diphosphide are obtained when ammonia acts on the diphosphide—*vide supra.* They found that **hydrogen hemienneaphosphide,** P_9H_2, is formed when the diphosphide is warmed in air at 175°: $5P_{12}H_6=6P_9H_2+6PH_3$; and when the black ammonium salt—*vide supra*—is heated to 200° in vacuo, or warmed with dil. hydrochloric acid. The hemienneaphosphide is either a red flocculent powder or a red vesicular mass, according as the temp. is raised slowly or rapidly during the decomposition of the diphosphide; it is stable in dry air, but in moist air it rapidly increases in weight, acquires an acid reaction, and becomes converted into phosphine and phosphoric acid; it is darkened by contact with alkalies in the cold, and, on warming, dissolves with evolution of phosphine, but it dissolves readily in dry liquefied ammonia without the formation of phosphine. Prolonged heating in a high vacuum at 340°–360° converts it into red phosphorus.

According to L. Hackspill, when one of the alkali phosphides of the type M_2P_5 is treated with dil. acetic acid, yellow **hydrogen hemipentaphosphide**, H_2P_5, is produced; and the same compound is formed when the hemienneaphosphide is heated in vacuo at 80° for several hours The hemipentaphosphide is considered to be of an acid nature, and the phosphides M_2P_5 to be salts of that acid.

U. J. J. Leverrier, and A. Gautier noted that when phosphorus is half covered with phosphorous chloride, and exposed to air, the aq. soln. so obtained decomposes at 80° into free phosphoric acid, and yellow flocks of a substance regarded as a hydrated suboxide; B. Francke reported the same substance to be formed by gradually adding phosphorus subiodide, P_4I_2, dissolved in carbon disulphide, to water. The water becomes yellow owing to the formation of **hydrogen hydroxytetraphosphide hydroiodide.** The carbon disulphide layer becomes colourless. When the aq. soln. is heated to 80° it becomes colourless, and deposits yellow flocks of **hydrogen hydroxytetraphosphide**, $P_4H.OH$. This substance decomposes slowly under water, more rapidly in moist air, forming phosphorus, phosphine, and hypophosphorous acid. It dissolves in alcoholic potash with the evolution of hydrogen, forming **potassium oxyhydrotetraphosphide**, $P_4H.OK$, which is very quickly decomposed by water: $3P_4H(OK)+6H_2O+3KOH=6KH_2PO_2+2PH_3+4P$. The potassium salt is formed when alcoholic potash-lye acts on hydrogen diphosphide: $P_4H_2+KOH=H_2+P_4H.OK$. The action of dil. potash-lye on phosphine furnishes *potassium oxydihydrophosphide*, PH_2OK, thus: $PH_3+KOH=PH_2OK+H_2$; and this immediately decomposes: $4PH_2OK=P_4H_2+H_2+4KOH$.

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§ 12. The Metal Phosphides

Phosphorus unites with most of the metals, forming phosphides. Phosphorus is electronegative towards hydrogen, and its affinity for the metals is rather less than that of sulphur. The phosphides are made by the direct union of the two elements usually assisted by heat, and in an atmosphere of an inert gas to prevent undue oxidation. In this way, at a dull red-heat, the metals iron, nickel, cobalt, copper, manganese, palladium, platinum, and iridium united with phosphorus with incandescence; and gold, silver, tin, and zinc without incandescence. Phosphides are also made by heating the metal or metal salt (halides) or metal oxide in a stream of phosphine or phosphorus halide; by passing phosphine through aqueous soln. of the metal salts, or by the action of a soln. of phosphorus in carbon disulphide on a metal salt—the phosphides of arsenic, antimony, and bismuth have been made in this way. Phosphides have also been made by reducing a phosphate with hydrogen or charcoal; and by heating the metal with copper phosphide in an electric furnace. The phosphides of the strongly electropositive metals—like potassium and calcium—behave like weak salts, and they are readily hydrolyzed by water, forming a hydroxide or hypophosphite of the metal and phosphine; on the other hand, the phosphides of the weaker electropositive metals—*e.g.* iron and copper—have characters like the metals, and are closely related with alloys; they are not decomposed by water, but some are decomposed by warming with dilute acids. Nitric and hypochlorous acids convert many phosphides into orthophosphates. The subject generally wants overhauling since many of the alleged phosphides hold a precarious position in the list of chemical individuals.

L. Troost[1] inferred that a **lithium phosphide** is formed when lithium is exposed to the vapour of phosphorus, because the product gives off phosphuretted hydrogen when treated with water; and H. Moissan made a similar observation with respect to the product of the action of phosphorus vapour on lithium carbide. Some analogous qualitative observations were made by H. Davy, J. L. Gay Lussac and L. J. Thénard, G. Magnus, H. Rose, E. Tomkinson and G. Barker, and F. Berlé on the production of **potassium and sodium phosphides** when the vapour of phosphorus, or phosphine is passed over the heated alkali metal; by P. Vigier, when the two elements are fused together under petroleum and the excess of phosphorus removed by washing with carbon disulphide; by R. Bunsen, and J. L. Gay Lussac and L. J. Thénard, when the alkali metal is heated with phosphoric acid or a phosphate. T. de Grotthus also made impure alkali phosphide by the action of phosphine on alcoholic potassium hydroxide.

According to C. Hugot, when liquid ammonia is brought in contact with a mixture of potassium or sodium and red phosphorus, the sodammonium or potassammonium first formed is decomposed by the phosphorus with the liberation of hydrogen; potassium yields a red compound, **potassium triamminopentaphosphide,** $KP_5.3NH_3$, which, when heated to 180°, loses all its ammonia, and leaves a brown mass of **potassium pentaphosphide,** KP_5. Sodium, under similar conditions, furnishes **sodium triamminotriphosphide,** $NaP_3.3NH_3$, and at 180°, **sodium triphosphide,** NaP_3. The potassium compound is not quite pure on account of the slight solubility of potassamide in liquid ammonia; this phenomenon does not occur with the sodium compound. Both phosphides are decomposed by moist air with the liberation of hydrogen phosphide.

According to A. Joannis, when hydrogen phosphide is passed into a soln. of potassammonium in liquefied ammonia, the gas is absorbed and hydrogen is evolved, a liquid being formed which does not mix with the ammonia, although not quite insoluble in it. When the action is complete, and the excess of ammonia is allowed to volatilize, *potassium dihydrogen phosphide* or *potassium phosphine,* or **potassium phosphamide,** PH_2K, is obtained in slender, white needles. When heated, it is converted into **potassium tritaphosphide,** PK_3, with evolution of hydrogen phosphide, and water also decomposes it with evolution of hydrogen phosphide. Sodammonium behaves similarly, the quantity of hydrogen liberated corresponding with the formation of **sodium phosphamide,** PH_2Na. The liquid solidifies when slowly cooled. If, however, the tube is kept at 0° and the ammonia is allowed to escape, a considerable quantity is retained by the phosphide, and the liquid does not solidify. No definite compound of the phosphide and ammonia seems to be formed, and a further quantity of the latter is evolved when the liquid is allowed to acquire the ordinary temp. If it is heated at 65°, still more ammonia is liberated, and the residue solidifies, and has the composition sodium phosphamide, PH_2Na. It decomposes in the same manner as the potassium compound, furnishing

sodium tritaphosphide, Na_3P. When nitrous oxide is allowed to act on them derivatives of phosphine, a volume of nitrogen is liberated equal to the volume of nitrous oxide employed, and the action is therefore quite different from that between nitrous oxide and the amides. If a mixture of red phosphorus and sodium be left in contact with liquid ammonia, yellow crystalline sodium phosphinotritaphosphide, $Na_3P_2H_3$, or $Na_3P.PH_3$, is formed simultaneously with phosphine, and sodamide. If an excess of sodium is not used, sodium phosphamide, PH_2Na, is produced. The phosphinotritaphosphide is decomposed by acids and by water with the liberation of phosphine, and when heated above 180°, it loses phosphine and hydrogen; at 150°–200°, less phosphine; and at 200°–300°, hydrogen alone.

H. Moissan made qualitative observations on the formation of **rubidium phosphide** by the action of molten phosphorus on rubidium hydride; and likewise on **cæsium phosphide.** L. Hackspill and R. Bossuet prepared a series of alkali phosphides with the general formula M_2P_5, by distilling successively 2–3 grms. of metal and a large globule of phosphorus into an evacuated tube, and heating the mixture to 400°–430°—with sodium, a temp. of 450° is necessary. A black mass is formed containing the free metal, but after heating for 100–150 hrs. this is volatilized, and the reddish-brown phosphide remains. In this way, they obtained **sodium hemipentaphosphide,** Na_2P_5; **potassium hemipentaphosphide,** K_2P_5, of sp. gr. 2; **rubidium hemipentaphosphide,** Rb_2P_5; and **cæsium hemipentaphosphide,** Cs_2P_5. At 0°–100°, the four phosphides resemble cadmium sulphide in appearance, but become darker at higher temp., and are almost colourless when cooled in nitrogen. They melt near 650° with decomposition and the loss of phosphorus; they decompose in air; and when treated with water yield a solid hydrogen phosphide together with a little phosphine and hydrogen. L. Hackspill found that with very dil. acetic acid, the yellow solid is hydrogen hemipentaphosphide, H_2P_5, and this is considered to be the acid parent of the phosphides M_2P_5. The rubidium salt was found by L. Hackspill and R. Bossuet to form a limpid soln. with liquid ammonia, which on evaporation at —18° deposits yellow, transparent crystals of **rubidium pentamminohemipentaphosphide,** $Rb_2P_5.5NH_3$. This phosphide effloresces with the loss of ammonia at ordinary temp.; it dissolves in liquid ammonia, and the soln. reacts with liquid ammonia soln. of the nitrates of barium, strontium, calcium, silver, copper, and lead, forming amorphous precipitates, yellow in the case of the alkaline earth metals, brown with silver, and black with the others.

W. B. Schober and F. W. Spanutius[2] have reported the preparation of salts of the phosphorus analogue of hydrogen cyanide. When phosphine is passed over heated sodium, PH_2Na, or Na_2HP, or Na_3P, is formed, the reaction is possibly analogous with the action of ammonia on sodium: $2Na+2NH_3=2NH_2Na+H_2$; when sodamide, $NaNH_2$, is treated with carbon monoxide, sodium cyanide is formed: $NaNH_2+CO=NaCN+H_2O$, and when the corresponding derivative of phosphine is treated in a similar way, **sodium phosphocyanide,** NaCP, is formed: $NaPH_2+CO=NaCP+H_2O$. The compound is very unstable, it gives off phosphine and forms formic acid: $NaCP+2H_2O=PH_3+H.COONa$, when treated with water.

Some general remarks on the combination of copper and phosphorus were made in connection with the action of phosphorus on copper—**3.** 21, 6—and **copper phosphides** with Cu : P in the at. proportions 3 : 1, 5 : 2, 2 : 1, 3 : 2, 1 : 1, and 1 : 2 have been reported at various times. These compounds, or rather alloys, were observed towards the end of the eighteenth century by A. S. Marggraf,[3] B. Pelletier, and B. G. Sage. The relation of copper to phosphorus is important because it is largely concerned with the production of the so-called phosphor-bronzes obtained by H. de Ruolz-Montchal and H. de Fontenay about 1854. The effect of copper on these alloys is discussed in connection with the properties of the alloys of tin —**7.** 46, 5. Alloys have been made by the direct union of copper and phosphorus vapour—by B. Pelletier A. S. Marggraf,, R. Lüpke, E. Heyn and O. Bauer, F. A. Abel, A. Granger, A. Schrötter, H. H. Hvoslef, etc.; E. Casoria passed the vapour of phosphorus over cuprous chloride or nitrate; by heating a mixture of copper and carbon with phosphoric acid or a phosphate—by B. Pelletier, B. G. Sage, P. Berthier, H. Schwarz, C. Künzel, P. Mellmann, etc.; by heating mixtures of copper oxide, phosphorus, and carbon—by G. Seyboth; by heating copper phosphate admixed with carbon—by P. Berthier, L. Gnétat and J. Chavanne, C. Matignon and R. Trannoy, etc.; by treating soln. of copper salts with phosphorus—by R. Böttger, A. Oppenheim, A. Joannis, etc., by the electrolysis of molten phosphates or phosphoric acid, using copper electrodes—by H. Davy, H. N. Warren, P. Burckhard, L. Dill, etc.; and by the electrolysis of soln. of copper salts—E. Goerke, R. Böttger, D. S. Ashbrook, O. N. Heidenreich, etc. T. Sidot made some general observations on the crystals; B. G. Sage, and H. de Ruolz-Montchal and H. de Fontenay, on the sp. gr. and hardness; W. R. Webster and co-workers, on the mechanical properties; A. Matthiessen and C. Vogt, on the electrical conductivity; and other observations on the properties have been indicated, **3**. 21, 6. A. Rietzsch measured the thermal and electrical conductivities. The chemical properties were discussed by A. Granger, E. Heyn and O. Bauer, H. Moissan, F. A. Abel, R. Lüpke, W. G. Otto, etc. G. Tammann and H. Bredemeier studied the rate of thickening of films produced on copper phosphide when exposed to oxygen and to the halogens. What appeared to be a **colloidal copper phosphide** was obtained by W. Straub by the joint action of copper, phosphorus, and water in air. A. Granger concluded:

> The quantity of metalloid retained by the metal augments with the duration of heating, and that it tends towards a limit established by a definite compound, which may be reached if the experiment be sufficiently prolonged. Thus the phosphide approaching Cu_2P, at the temp. of formation, can be transformed into a crystalline compound Cu_5P, perfectly distinct both in its physical and chemical properties from alloys more or less resembling Cu_3P.

And E. Heyn and O. Bauer:

> (i) Alloys with more than 15 per cent. phosphorus cannot be prepared by fusion. On the other hand, copper-phosphorus alloys richer in phosphorus are prepared by heating copper turnings and phosphorus at a lower temperature (300°–400°). A proposal is made to apply these facts to the technical production of phosphor-copper. (ii) At higher temperatures those alloys richer in phosphorus (15·0 per cent.) lose phosphorus. To every temperature corresponds a definite phosphorus content, which is reached as a limiting condition by loss of phosphorus. At 1100°, this saturation phosphorus content is 14·1 per cent., corresponding to a compound Cu_3P. (iii) In rapid heating and melting of phosphorus-rich alloys there is not sufficient time to reach the saturation phosphorus content by loss of phosphorus. To this fact is due the possibility of technically producing by fusion alloys containing up to 15 per cent. of phosphorus. The alloys with over 14·1 per cent. phosphorus form mixed crystals of the compound Cu_2P and a second compound, probably Cu_3P_2. The γ solid soln. has, with phosphorus over 14·3 per cent., the same melting point, 1022°. This temperature corresponds to the boiling point of melts which are saturated γ soln.

C. A. Edwards and A. J. Murphy measured the rate at which copper reacts with phosphorus vapour between 600° and 700°, and referred the results to the expression $dw/dt=kA/D$, where k is a constant; w denotes the number of grams converted into phosphide in the time t min.; A, the area of the exposed copper in sq. cm.; and D, the depth in cm.

	t	D	A	dw/dt	k
600°	10	0·023	7·447	0·120	0·000371
	30	0·0515	6·625	0·044	0·000345
	60	0·069	6·250	0·03	0·000331
640°	15	0·053	6·603	0·20	0·00160
	30	0·080	6·013	0·111	0·00147
	60	0·123	4·985	0·04	0·00107
700°	10	0·106	5·507	0·40	0·00770
	30	0·203	3·68	0·133	0·00730
	60	0·267	2·691	0·033	0·00327

The results for k are very fair at 600° and 640°, but not so for the 60-minute observation at 700°. P. E. Demmler gave 400° as the most satisfactory temp. for phosphorizing copper; but C. A. Edwards and A. J. Murphy showed that 640° is nearer the mark.

It has been possible to examine only a portion of the equilibrium curve because copper cannot hold much over 14 per cent. of phosphorus at a red-heat. F. A. Abel, and A. H. Hiorns worked with alloys containing up to 14 per cent. of copper. A. Granger said that phosphorus begins to act on copper at about 400°, and at about 600°, the copper can take up between 29 and 30 per cent. of phosphorus, while E. Heyn and O. Bauer made an alloy with 20 per cent. of phosphorus at 700°—but in all cases the phosphorus is expelled at a higher temp. P. E. Demmler, A. K. Huntington and C. H. Desch said that at ordinary press. 15 per cent. of phosphorus is the limit dissolved, and A. E. Tucker found that with alloys containing this amount of phosphorus, some of the red variety of that element is present in a free state. A. H. Hiorns' values for the f.p. of some alloys with up to 14 per cent. of phosphorus are as follow:

P . .	0	0·25	4·11	5·75	8·21	9·03	10·67	12·00	13·00	14·00
F.p. . .	1082°	1070°	1050°	820°	620°	650°	795°	950°	990°	1005°

E. Heyn and O. Bauer's f.p. curve is shown in Fig. 21. A. H. Hiorns gave 620° for the eutectic temp. with 8·2 per cent. of phosphorus. The f.p. of copper is steadily depressed by additions of phosphorus from the f.p. of pure copper to that of the eutectic; the f.p. curve then rises to the saturation point with 14 per cent. of copper. The eutectic alloy shows the characteristic pearlitic structure; with copper in excess, the metal shows islands of copper surrounded by the eutectic matrix; and with an excess of phosphorus, crystals of **copper tritaphosphide,** Cu_3P, also surrounded by the pearlitic eutectic matrix. The complete diagram has not been worked out, but E. Heyn and O. Bauer discussed the diagram for the case of a system of two elements, A and R, which form two compounds, V_1 and V_2, which give a complete homogeneous series of solid soln. γ. V_1 is supposed to boil without decomposition at *G*, while V_2 does not boil without decomposition. C. A. Edwards and A. J. Murphy found that there is a line corresponding with *CA* for the system: Cu–P.

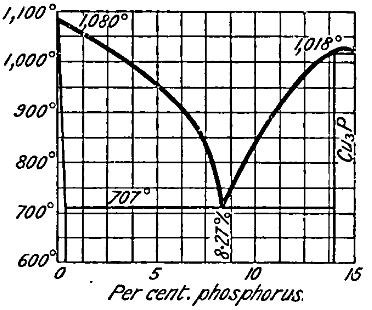

FIG. 21.—Portion of Freezing-point Curve of Copper-Phosphorus Alloys.

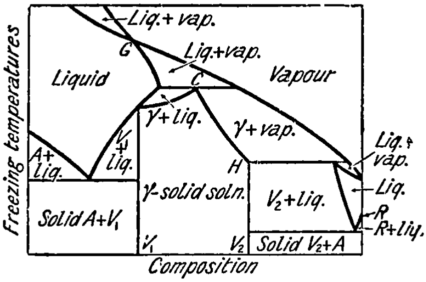

FIG. 22.—Imaginary Equilibrium Diagram of a Case like the System: Cu–P.

The tritaphosphide was analyzed by F. A. Abel, A. Granger, H. Rose, A. Schrötter, H. H. Hvoslef, and E. Rubenovitch. It is formed as indicated above, and, according to F. A. Abel, and A. Granger, when phosphorus vapour is passed over copper at about 900°. H. Rose, A. Granger, A. Schrötter, H. H. Hvoslef, and E. Heyn and O. Bauer obtained it by heating higher phosphides to say 1100°. A. K. Christomanos obtained it by the action of an ether or benzene soln. of phosphorus on an excess of an aq. soln. of cupric nitrate; E. Priwoznik, by reducing cupric phosphate with charcoal at a high temp.; and J. Riban, by heating cuprous phosphinochloride. E. Rubenovitch said that it is formed when phosphine acts on copper in the absence of air—the reaction begins at 180°–200°, and is completed below the decomposition temp. of phosphine; he also obtained it by the action of phosphine on precipitated cuprous oxide in ammoniacal soln. of various cupric salts, or cupric hydroxide ; P. Kulisch, by the action of phosphine on a mixed soln. of cuprous and sodium chlorides ; and H. Rose, by the action of phosphine on heated cuprous chloride or sulphide. The tritaphosphide is a steel-grey mass with a crystalline fracture, or a grey powder. H. H. Hvoslef obtained it as a silvery-white mass. A. Schrötter gave 6·75 for the sp. gr., and H. H. Hvoslef, 6·59. E. Priwoznik found it to be harder than copper or wrought iron, but softer than steel ; and E. Heyn and O. Bauer said it is about as hard as annealed steel. G. Pfleiderer studied the thermal and electrical conductivities of copper-phosphorus alloys. The tritaphosphide, said E. Priwoznik, can be kept for a long time in air without change, while P. Kulisch found it to be slowly oxidized by exposure to air. E. Rubenovitch said that it is rapidly oxidized in air or in oxygen at 100°. When heated on charcoal H. Rose said that the phosphorus burns with a green flame. These different observers found the tritaphosphide to be slowly dissolved by nitric acid, forming phosphoric acid ; it dissolves slowly in aqua regia ; H. Rose said that it is insoluble in hydrochloric acid, but A. Schrötter said it does dissolve slowly in that acid ; hot conc. sulphuric acid forms phosphine, sulphur dioxide, and maybe some sulphur. G. Tammann and H. Bredemeier studied the surface oxidation of copper phosphide. E. Rubenovitch found the tritaphosphide dissolves easily in bromine water ; and does not reduce potassium permanganate soln.

A. Granger made **copper dipentitaphosphide,** Cu_5P_2, by passing the vapour of phosphorus trifluoride or trichloride over copper at a red-heat ; E. Rubenovitch made the same product by the action of a slow current of phosphine (alone or diluted with an inert gas) at a low temp. on copper carbonate or hydroxide, or on cuprous oxide suspended in water ; and J. B. Senderens made it by the action of red phosphorus on a dil. soln. of cupric nitrate. This phosphide forms steel-grey, hexagonal, prismatic crystals which are transformed into the phosphate on exposure to moist air. The dipentitaphosphide passes into cuprous phosphide and free copper when heated to redness. The crystals dissolve in nitric acid, and in bromine water, and they reduce potassium permanganate. Hot conc. sulphuric acid is reduced to sulphur dioxide and sulphur. E. Rubenovitch prepared a black precipitate of what appears to be monohydrated copper dipentitaphosphide by the action of a mol of phosphine (from phosphonium iodide) on an aq. soln. of two mols of copper sulphate. E. Rubenovitch thinks that it is possible that this supposed compound is a mixture or double compound of the two phosphides Cu_3P and Cu_3P_2.

A. Granger reported the formation of **copper hemiphosphide,** Cu_2P, by passing the vapour of phosphorus, diluted with an inert gas, over copper heated to about 650°–700° ; and G. Maronneau, by heating a mixture of calcium phosphate and carbon in an electric arc furnace. The compound was reported by A. Schrötter and H. H. Hvoslef to be formed by the action of the vapour of phosphorus on heated copper, but these directions are too vague to enable the experiments to be repeated ; the same remark applies to F. Casoria's statement that the compound is formed by the action of phosphorus vapour on soln. of cupric salts, or by boiling phosphorus with soln. of these salts. The formula is in agreement with the analyses of A. Granger, and G. Maronneau. Copper hemiphosphide is a grey mass with a metallic appearance, and difficult to powder. G. Maronneau found the sp. gr. to be 6·4. It loses phosphorus when heated to bright redness. In moist air it loses its lustre, and oxidizes when heated in air. Some phosphorus is expelled at 1000° in hydrogen ; fluorine attacks it with a glow at ordinary temp., and cold chlorine, bromine, or iodine, as well as other oxidizing agents attack it. At dull redness, iodine forms phosphorus pentaiodide and a phosphide ; melted sulphur forms copper sulphide. It is soluble in hot nitric acid, the cold acid acts very slowly ; hot hydrochloric and sulphuric acids attack it slowly, forming in the latter case sulphur and sulphur dioxide. It is not attacked by cold or hot acetic or hydrofluoric acid ; and it is soluble in aqua regia, and in a mixture of hydrofluoric and nitric acids.

H. Rose reported **copper ditritaphosphide**, Cu_3P_2, to be formed when phosphine is passed over heated cupric chloride, or through a soln. of cupric sulphate. This precipitate was also observed by J. B. A. Dumas, H. Buff, and G. Landgrebe, who regarded it simply as a phosphide; E. Rubenovitch, and P. Kulisch regarded it as a mixture. R. Böttger said that if yellow phosphorus is boiled with a repeatedly renewed soln. of cupric sulphate, or acetate, a mixture of phosphide and basic sulphate or acetate is formed; when the washed product is digested with a soln. of potassium dichromate acidified with sulphuric acid, there remains the ditritaphosphide. Red phosphorus forms only a superficial film of this phosphide; a soln. of cupric chloride will not do because it is simply reduced to cuprous chloride. A. K. Christomanos obtained it by the action of a soln. of phosphorus in ether or benzene on a not too dil. aq. soln. of cupric nitrate not in excess. H. Moissan obtained it by the action of phosphorus vapour in an atm. of nitrogen or carbon dioxide, on copper at a dull red-heat; and B. Reinitzer and H. Goldschmidt, by passing phosphoryl chloride or phosphorus trichloride over copper at 250°—phosphorus pentachloride forms cuprous chloride and phosphorus trichloride; and phosphoryl chloride gives a number of by-products, cupric chloride, phosphorus pentoxide, and trioxytetrachloride. The compound was analyzed by H. Moissan, H. Rose, T. Parkman, and R. Böttger. A. K. Christomanos obtained the ditritaphosphide in black flocks, and in black, needle-like crystals; usually it appears as a black powder, which, according to G. Landgrebe, melts more easily than copper, but it is probable that the ditritaphosphide was decomposed during the fusion, for H. Rose said that when heated to redness in hydrogen it loses half its phosphorus; T. Sidot, and H. Moissan also noticed that phosphorus was lost when this phosphide is heated in a test-tube. T. Sidot gave 6·350 for the sp. gr., and found that the finely-divided ditritaphosphide burns vigorously in chlorine. R. Böttger said that when heated with iodine and water it forms cuprous iodide, and hydriodic and phosphoric acids; if the ditritaphosphide prepared at the high temp. be treated with hydrochloric acid, it does not readily dissolve, but that prepared at a low temp. dissolves more easily than copper in the presence of air; and when boiled cuprous chloride and phosphine are formed. R. Böttger said that when the ditritaphosphide is mixed with potassium chlorate it detonates when struck with a hammer. The ditritaphosphide prepared at a high temp. is not attacked by sulphuric acid, but the low temp. form is dissolved by the hot acid giving off phosphine and sulphur dioxide; with nitric acid, phosphoric acid is formed. When a mixture with potassium nitrate is heated, detonation occurs. T. Sidot found that phosphine is given off when the ditritaphosphide is acted on by an aq. soln. of potassium cyanide.

O. Emmerling prepared **copper monophosphide**, CuP, by heating the two constituents in a sealed tube; A. Granger, by the action of phosphorus vapour on copper at 600°; H. Goldschmidt, by the action of phosphorus pentachloride on copper; A. Granger, and T. Sidot, by the action of a soln. of copper hydrophosphite on red phosphorus; H. Rose, and F. A. Abel, by heating in hydrogen copper phosphate precipitated by sodium hydrophosphate; and J. Katz, by shaking a soln. of phosphorus in carbon disulphide with a soln. of cupric sulphate; washing out the carbon disulphide with ether; and washing the precipitate with water, alcohol, and ether. A. K. Christomanos' repetition of J. Katz's process yielded only the ditritaphosphide. Analyses were made by O. Emmerling, A. Granger, H. Rose, J. Katz, and A. K. Christomanos. The grey product, said A. Granger, looks like graphite. It is quickly oxidized by air, especially when heated. F. A. Abel said that when heated in hydrogen it passes into the tritaphosphide. The monophosphide is attacked in the cold by chlorine and bromine; it is sparingly soluble in hydrochloric acid; freely soluble in nitric acid; aq. ammonia in air forms phosphate and phosphite; and it detonates when admixed with potassium nitrate or chlorate and struck with a hammer.

A. Granger reported **copper diphosphide**, CuP_2, to be formed when carbon dioxide charged with vapour of phosphorus trichloride, tribromide, or diiodide is passed over gently heated copper, the diphosphide is obtained as a crystalline solid with a colour and lustre resembling that of silicon. It is readily attacked by chlorine, bromine, or nitric acid, and more slowly by hydrochloric acid. When heated out of contact with air, it yields copper phosphide and phosphorus; heated in presence of air, it oxidizes, and when mixed with oxidizing agents such as potassium chlorate, it detonates when struck. Phosphorus trifluoride, under similar conditions, yields the dipentitaphosphide.

In 1792, B. Pelletier[4] dropped phosphorus on to silver heated to redness in a crucible, and found the metal instantly melted; he continued adding phosphorus until he believed the silver to be sat. The molten mass had a tranquil surface, but, on cooling, much phosphorus was emitted, and the surface became *toute mamelonnée* owing to the spitting of the silver as it rejected the phosphorus in soln. It was estimated that the solid silver retained about 15 per cent. of phosphorus, and that it lost 10 per cent. in the act of solidification. J. Percy found a maximum of 0·293 per cent. to be retained by the solid metal. P. Hautefeuille and A. Perrey, and H. N. Warren confirmed these observations in a general way. H. André observed that fused silver phosphides absorb phosphorus vapour, and the electrical resistance then decreases regularly with a rise of temp. A direct current slowly displaces the silver, but an alternating current has no perceptible effect at low temp. In addition to the formation of a **silver phosphide** by the direct union of the elements, B. Pelletier observed that a silver phosphide is formed by melting silver with metaphosphoric acid and charcoal; and G. Landgrebe obtained a phosphide by heating silver orthophosphate with charcoal. For the action of phosphine on silver nitrate resulting in the formation of **silver nitratophosphide,** $Ag_3P.3AgNO_3$, *vide* **3.** 22, 21—the action of phosphine on silver nitrate. According to R. Fresenius and H. Neubauer, carbon dioxide charged with phosphorus vapour forms a similar product; and, according to J. B. Senderens, solid phosphorus reacts with a neutral soln. of silver nitrate, or, according to A. Oppenheim, with an ammoniacal soln. of silver oxide furnishing either free silver, or a mixture of silver and silver phosphide. O. Emmerling reported that **silver monophosphide,** AgP, is formed by heating silver and phosphorus in an evacuated sealed glass tube; when the product was heated in air, silver remained as a residue while phosphorus was evolved. A. Schrötter reported **silver hemiphosphide,** Ag_2P_3, or Ag_4P_6, to be formed by heating finely-divided silver in phosphorus vapour; the product was said to be insoluble in hydrochloric acid, but freely soluble in nitric acid. According to A. Granger, **silver diphosphide,** AgP_2, is produced when reduced silver is heated in phosphorus vapour at 400°, or when phosphorus acts on silver chloride at 400°. The diphosphide is said to give off phosphorus in a current of an indifferent gas at 500°, and to form a new phosphide at 900°. The diphosphide is soluble in nitric acid; and is attacked by aqua regia, and by chlorine and bromine. E. Boissuet and L. Hackspill treated a soln. of rubidium hemipentaphosphide in liquid ammonia with silver nitrate and obtained a brown easily oxidizable precipitate thought to be **silver hemipentaphosphide,** Ag_2P_5.

The affinity of gold for phosphorus is small. P. Hautefeuille and A. Perrey[5] noticed that molten gold absorbs the vapour of phosphorus, and spits it out again on cooling. B. Pelletier noticed that by melting gold with glacial phosphoric acid and charcoal, a yellow alloy of gold with about 4 per cent. of phosphorus was obtained; and E. Davy prepared a grey-coloured alloy with 14 per cent. of phosphorus by heating gold with phosphorus in an evacuated sealed glass tube. By passing phosphine into an aq. soln. of auric chloride, a black precipitate is obtained which C. P. Oberkampf regarded as gold phosphide, but H. Rose as metallic gold. A. Cavazzi reported the precipitation of **gold monophosphide,** AuP, when dried phosphine mixed with the vapour of ether is led into an ethereal soln. of auric chloride free from water. The brown hygroscopic powder decomposes in air, forming the acids of phosphorus; and it is blackened when kept 7 or 8 days in vacuo. It burns in air at 100°–110°, forming metallic gold; and in a current of carbon dioxide at a red-heat it loses all its phosphorus. This phosphide is decomposed by cold or hot water, forming phosphoric acid and metallic gold; potash-lye acts like water but more energetically. The monophosphide inflames by contact with fuming nitric acid; and it is decomposed by dil. nitric acid, forming phosphoric acid, and giving off nitric oxide and nitrogen peroxide. Cold conc. sulphuric has no action, but the hot acid forms gold, phosphoric acid, and sulphur dioxide. A. Schrötter reported grey-coloured **gold hemitriphosphide,** Au_2P_3, or Au_4P_6, to be formed by heating gold in phosphorus vapour, but A. Granger could not confirm this, and obtained instead what he considered to be Au_3P_4 by heating finely divided gold in phosphorus vapour to about 400°; but which decomposes at a higher temp. It also decomposes when heated in air or in carbon dioxide, and is readily attacked by aqua regia or by chlorine.

A kind of *phosphated lime*, a mixture of calcium phosphide and calcium pyrophosphate, was made by the action of the vapour of phosphorus on red-hot lime by G. Pearson,[6] S. L. Mitchill, H. Rose, J. B. A. Dumas, and P. Thénard, and used for the preparation of the hydrogen phosphides (*q.v.*). Normal **calcium phosphide,** Ca_3P_2, was made by P. Vigier by melting phosphorus and calcium together under petroleum, as in the case of the alkali phosphides. The Chemische Fabrik Griesheim-Elektron made it by heating calcium carbide with phosphoric oxide. A. Renault, and H. Moissan prepared it by heating an intimate mixture of calcium phosphate and lamp-black for 3 or 4 minutes in an electric arc furnace. The product is a reddish-brown crystalline mass, whereas the phosphide obtained by passing phosphorus vapour over calcium in vacuo at dull redness is amorphous. The sp. gr. is 2·51 at 15°. It melts with difficulty in the electric furnace, and if the action of the arc is continued too long, some phosphide is decomposed. Calcium phosphide is not affected by hydrogen or nitrogen at 900°, but at 1200° is slightly decomposed by the latter, and a small quantity of nitride is formed. Boron and carbon are without action; at a higher temp., carbon converts it into calcium carbide. Arsenic has no action at the softening temp. of glass. Chlorine has no action on the phosphide in the cold, but attacks it readily at about 100°, and bromine and iodine behave in the same way at somewhat higher temperatures. Oxygen and sulphur decompose the phosphide with incandescence at about 300°. Oxidizing agents, including nitrous and nitric oxides, attack it very readily at a red-heat, and the halogen hydracids decompose it with great energy. Concentrated nitric and sulphuric acids are without action, but in presence of water the phosphide is rapidly decomposed. Water acts somewhat slowly on the crystallized phosphide, and if it has been heated sufficiently in the electric furnace, the liberated hydrogen phosphide is not spontaneously inflammable; the reaction is complex, and all the phosphorus is not liberated in the form of hydride. J. A. Hedvall and E. Norström found that barium oxide begins to react with calcium phosphide at 331°; and strontium oxide at 447°. Calcium phosphide was found by H. P. Cady and R. Taft to be insoluble in liquid sulphur dioxide. Ordinary organic solvents have no action on the phosphide.

A. Jaboin prepared normal **strontium phosphide,** Sr_3P_2, in a similar manner, by heating an intimate mixture of lamp-black and strontium phosphate in the electric arc furnace for 3–4 minutes. The sp. gr. is 2·68, and it melts only at the high temp. of the electric furnace. Strontium phosphide burns in fluorine at the ordinary temp., in chlorine at about 30°, in bromine at 170°–175°, in iodine at a red-heat, in oxygen above 300°, and in sulphur vapour at a higher temperature. It is decomposed by carbon at a high temp., but not by sodium at a red-heat; by dilute acids and gaseous hydracids, but not by concentrated acids, nor by hydrogen sulphide or ammonia, nor by organic solvents. It alters rapidly in moist air, is decomposed by water with liberation of hydrogen phosphide, and is violently attacked by oxidizing agents. A *phosphated baryta*, analogous to phosphated lime, was prepared by J. B. A. Dumas, and P. L. Dulong. A. Jaboin obtained normal

barium phosphide, Ba_3P_2, by a method similar to that employed for the strontium compound. The product was a black crystalline mass of sp. gr. 3·183. The properties are similar to those of strontium phosphide, but it is not so active chemically; it burns in chlorine at 90°, but in bromine vapour at 260°–300°.

F. Wöhler[7] obtained an impure **beryllium phosphide** by heating beryllium in the vapour of phosphorus; the reaction proceeds with incandescence; and the grey pulverulent product develops phosphine when treated with water. More or less impure **magnesium phosphide,** Mg_3P_2, was obtained by R. Bunsen,[8] and L. Schönn by heating magnesium with dehydrated organic or inorganic substances containing phosphorus. The product evolves phosphine when treated with water. The phosphide was made by T. P. Blunt, by passing the vapour of phosphorus in a current of carbon dioxide over heated magnesium. The product was contaminated with carbon from the reduction of the carbon dioxide; accordingly, J. Parkinson, and H. Gautier used hydrogen in place of that gas. J. Parkinson, O. Emmerling, and R. Lüpke made magnesium phosphide by heating a mixture of magnesium filings and red or yellow phosphorus to redness in a glass vessel. Analyses by T. P. Blunt, J. Parkinson, and H. Gautier are in agreement with the above formula. The dark grey product is hard and brittle, and very difficult to fuse; and H. Gautier obtained small greenish-grey crystals which are rapidly decomposed by moist air. All observers noted the instability of the compound in moist air, and J. Parkinson said that phosphine is evolved and magnesium hydroxide with traces of phosphite and hypophosphite are formed. H. Gautier said that the phosphide can be preserved only in sealed tubes. J. Parkinson found that when heated in air it is oxidized superficially. H. Gautier reported that dry air and oxygen are without action at the ordinary temperature, but the phosphide burns in oxygen at a dull red-heat, and is converted into magnesium phosphate. Water very readily decomposes the phosphide, with production of magnesium hydroxide and pure hydrogen phosphide. The phosphide burns brilliantly when heated in chlorine, and also in bromine and iodine vapours at somewhat higher temperatures. Hydrochloric acid decomposes it with liberation of hydrogen phosphide; concentrated sulphuric acid slowly converts it into magnesium sulphate and phosphoric acid; nitric acid oxidizes it with incandescence, forming magnesium nitrate and phosphoric acid.

The union of molten zinc with phosphorus to form a **zinc phosphide** was observed by B. Pelletier,[9] E. A. Lewis, E. Baudrimont, and G. Landgrebe; F. Wöhler observed the formation of a zinc phosphide when zinc is heated with fused microcosmic salt; C. Trommer, when zinc and carbon are heated with phosphoric acid; H. H. Hvoslef, when zinc oxide is heated in phosphorus vapour; H. Rose, by the action of phosphine on zinc chloride; and H. H. Hvoslef, A. A. Proust, F. Selmi, and B. Reinitzer and H. Goldschmidt, by heating zinc in the vapour of phosphine diluted with nitrogen. The equilibrium diagram of the binary system has not been investigated. A. Schrötter reported normal zinc phosphide, or **zinc ditritaphosphide,** Zn_3P_2, to be formed by heating finely-divided zinc in the vapour of phosphorus. Combination sets in towards dull redness, and continues without incandescence; O. Emmerling used an analogous process. B. Renault used zinc oxide in place of zinc. P. Vigier added the phosphorus to molten zinc. R. Lüpke used a modification of this process; and P. Jolibois obtained it by heating zinc and phosphorus together in a crucible until fumes of phosphorus cease to be evolved. The product was fused from excess of zinc, either by ignition in vacuo at 600°, or by treatment with mercury or fuming nitric acid. J. J. Berzelius, and H. H. Hvoslef used a mixture of zinc or zinc oxide, phosphoric acid, and carbon; and B. Renault, a mixture of magnesium hydrophosphate, zinc sulphide, and carbon. The compound was analyzed by A. Schrötter, H. H. Hvoslef, and B. Renault. The normal phosphide appears as a steel-grey mass, which, if fused, consists of a mass of what H. Hager called *rhomboidischen Kristallen* of sp. gr. 4·72; A. Schrötter gave 4·76. P. Jolibois said the crystals are octahedral, and have a sp. gr. 4·55 at 13°. At a high temp., this phosphide may give off phosphorus without melting. B. Renault said that it melts at a higher temp. than zinc and volatilizes. P. Jolibois said the compound is infusible and sublimes in hydrogen at 1100°. It is not changed by air at ordinary temp., but if triturated in air it gives off the smell of phosphorus. If heated in air, it forms zinc phosphate. The phosphide is insoluble in zinc. R. Lüpke found that it is not attacked by water, but cold dil. hydrochloric and nitric acids were found by P. Sabatier to develop phosphine of a high degree of purity; and with nitrososulphuric acid it gives the blue soln. of nitrosodisulphonic acid.

H. H. Hvoslef heated a mixture of molten sodium hexametaphosphate and zinc turnings to redness in a retort; some phosphorus distils off, and there is formed a dark brown sublimate which is digested with boiling hydrochloric acid, and there remain grey plates with a metallic lustre with the composition of **zinc diphosphide,** ZnP_2. B. Renault obtained it by heating barium phosphide with zinc chloride; and by heating zinc oxide in phosphine. H. Rose seems to have obtained a similar product by the action of phosphine on zinc chloride. P. Jolibois made it by the action of phosphorus vapour on the normal phosphide at 400°, and digesting the product with dil. hydrochloric acid. The black powder has a sp. gr. 2·97 at 15°; it does not take up any more phosphorus at 400°, and at 500° it breaks down into phosphorus and the normal phosphide. It is not affected by conc. sulphuric acid, but it is slowly decomposed by conc. hydrochloric acid, forming gaseous and solid hydrogen phosphides.

B. Renault also claimed to have made *zinc monophosphide*, ZnP, in needle-like crystals during the preparation of the normal phosphide; *zinc tetratritaphosphide*, Zn_3P_4, as a red residue by treating the oxyphosphide with hydrochloric acid; and *zinc tetraphosphide*, ZnP_4, according to the analysis, as a yellow residue when the normal phosphide is treated with dil. hydrochloric acid. B. Renault also reported a *zinc oxyphosphide*, ZnP_2O, in orange-red needles in the sublimation of the normal phosphide, or of a mixture of zinc sulphide, carbon, and a phosphate. P. Vigier, and H. H. Hvoslef both considered the needle-like crystals to be phosphide not oxyphosphide.

According to E. Drechsel and E. Finkelstein, when a current of dry phosphine is passed into a soln. of zinc ethide in absolute ether, which must be cooled by a mixture of ice and salt, the separation of a white pulverulent precipitate is observed, which gradually increases in quantity. The precipitate was collected on a filter, washed rapidly with absolute ether, and dried in vacuo over sulphuric acid. The body thus obtained continually exhales phosphine when exposed to the air; its analysis corresponds with **zinc hydrophosphide.** The zinc hydrophosphide is decomposed at once by cold water, with evolution of phosphine and formation of zinc hydroxide. It is especially interesting for the ease with which it is attacked by chlorides and iodides; acetyl chloride acts upon it energetically, but the product of the reaction has not been thoroughly examined. By heating together the zinc hydrophosphide, ethyl iodide, and ether to 150°, ethyl-phosphine was produced.

F. Stromeyer,[10] and P. Vigier obtained a **cadmium phosphide** by the union of molten cadmium with zinc; while P. Kulisch obtained a phosphide by the action of phosphine on an ammoniacal soln. of cadmium sulphate. These products were not analyzed, but their chemical behaviour was characteristic of the metal phosphates. P. Drawe also found a cadmium phosphide in the residue obtained by the ignition of cadmium hypophosphate. O. Emmerling reported **cadmium hemiphosphide,** Cd_2P, to be formed when cadmium is heated for 12 hrs. with phosphorus. The grey or silvery-white mass consists of needle-like crystals associated with some red phosphorus. The product is soluble in hydrochloric acid with the evolution of phosphine. A. Oppenheim boiled cadmium oxide with an excess of phosphorus in potash-lye, and obtained pale brown, crystalline **cadmium ditritaphosphide,** Cd_3P_2. B. Renault obtained the same compound by the action of phosphorus vapour at a red-heat on cadmium, cadmium oxide, or cadmium carbonate; and A. Brukl obtained it as a black, unstable, flocculent precipitate by the action of phosphine on an ammoniacal soln. of cadmium sulphate. Dil. acids form non-spontaneously inflammable phosphine. He also obtained **cadmium diphosphide,** CdP_2, by heating ammonium phosphate, cadmium carbonate, and carbon; and as small red crystals in the preparation of the ditritaphosphide. Treatment of the diphosphide with acids gives phosphine, solid hydrogen phosphide, phosphoric acid, and a cadmium salt of the acid.

The affinity of mercury for phosphorus is small. According to D. Gernez,[11] molten phosphorus dissolves mercury, forming a colourless liquid which remains colourless until the temp. is raised, when the soln. blackens. B. Pelletier obtained a compound of mercury and phosphorus by heating mercury or mercuric oxide with phosphorus; H. Davy obtained a combination of the two elements by the action of phosphorus vapour on mercurous chloride; P. Boullay, by heating mercuric chloride with phosphorus; T. Thomson, by the action of phosphine on an aq. soln. of mercurous nitrate; and H. Rose, on solid mercuric chloride. A. Brukl obtained **mercurous phosphide,** Hg_3P, as a black, amorphous precipitate when hydrogen phosphide is allowed to react on a soln. of mercurous sulphate in dil. sulphuric acid; it is rapidly oxidized by the oxygen of the air, and gradually by dil. nitric acid. Phosphine is gradually evolved by the action of cold conc. hydrochloric acid, but much more rapidly by the action of the hot acid; with conc. sulphuric acid, sulphur dioxide is evolved. The compound is not explosive. A. Brukl also obtained **mercuric phosphide,** Hg_3P_2, by the action of a soln. of mercuric chloride in ether on hydrogen phosphide; it is a dark brown solid, becoming grey on exposure to air. In the cold, water, alkalies, and some dil. acids are without action, but on warming phosphine is evolved; it is oxidized in the cold by dil. nitric acid. A. C. Vournasos obtained a phosphide by heating the two constituents under molten paraffin; and A. C. Christomanos, by treating an ethereal or benzene soln. of phosphorus with mercurous or mercuric nitrate. A. Granger, and A. Partheil and A. van Haaren reported the formation of **mercury tetratritaphosphide,** Hg_3P_4, as a result of heating a mixture of mercury and phosphorus diiodide for 10 hrs. in a sealed tube at about 300°; and also by leading the vapour of the diiodide in a stream of inert gas over mercury; but it is not formed by the action of phosphine on dry or on an ethereal soln. of mercuric chloride. A. Partheil and A. van Haaren found that when phosphine is passed over dry mercuric chloride, the hydrogen chloride which is evolved does not correspond with the formation of mercury ditritaphosphide. T. de Grotthus obtained an impure phosphide by the action of phosphine on a mercury salt. According to A. Granger, the tetratritaphosphide forms brown rhombohedral crystals, which are stable when cold, but decompose into their constituents when heated. It inflames when heated in air, and in chlorine at ordinary temp. Mixed with potassium chlorate, it detonates by percussion. Nitric and hydrochloric acids separately have no action, but it is easily soluble in aqua regia. A. Partheil and A. van Haaren heated the phosphide with alkyl iodides in a sealed tube, and obtained tetralkylphosphonium compounds, *e.g.* $P(C_2H_5)_4.I\cdot 2HgI_2$; $P(CH_3)_4.I\cdot 2HgI_2$; etc. They also found that when purified phosphine is passed into a 2·5 per cent. alcoholic soln. of mercuric chloride, a dark brown precipitate is formed which is ultimately obtained free from chlorine; its composition is that of a **mercury oxyphosphide,** $Hg_5P_2O_4$—it is unstable. Some complex phosphides have been indicated in connection with the action of phosphine on mercury salts.

According to H. Moissan,[12] phosphorus does not react with amorphous boron at 750°; but G. Dragendorff obtained what appeared to be a compound of these elements by heating a mixture of borax and phosphorus; and A. Vogel obtained evidence of the existence of a compound of the two elements by heating boron phosphate, BPO_4, with sodium. H. Moissan, and A. Besson prepared **boron monophosphide,** BP, by heating the addition product, $PBr_3.PH_3$, to 300°, or boron phosphoiodide, BPI_2, or BPI, to about 500° in a stream of hydrogen. Boron phosphide is a maroon-coloured powder, insoluble in all the solvents which were tried; it is decomposed by boiling conc. alkali-lye with the evolution of phosphine.

Boiling water has no action on the phosphide, but it is decomposed by steam at 400°, forming boric acid and phosphine; conc. hydrochloric, hydriodic, or sulphuric acid has no action in the cold; hydrogen fluoride attacks the phosphide at a dull red-heat; and hydrogen iodide at a still higher temp. Boron phosphide inflames in conc. nitric acid, and fused alkali nitrates attack it with deflagration; it burns in oxygen at 200°, forming boric and phosphoric oxides; fused sulphur has no action, but it is attacked by sulphur vapour; hydrogen sulphide at a dull red-heat also attacks it, forming boron sulphide and hydrogen phosphide; chlorine reacts in the cold with incandescence; bromine when heated; and iodine has no action at dull redness. Nitrogen does not attack the phosphide at 500°; but the phosphide inflames when heated to 200° in ammonia gas, forming boron nitride and phosphorus. When heated with finely-divided metals, the phosphide is attacked. When boron phosphide is heated to about 1000° in a current of hydrogen, **boron tripentitaphosphide,** B_5P_3, is formed; this compound does not inflame in chlorine below a dull red-heat; it is not attacked by nitric acid, but it is attacked by fused nitrates.

According to H. Moissan, melted phosphorus acts with great energy on boron triiodide, and if red phosphorus is heated in the vapour of the iodide, decomposition takes place with incandescence. If, however, a soln. of the iodide in carbon disulphide is mixed with a similar soln. of phosphorus, great care being taken to avoid the presence of moisture, the reaction takes place more slowly. The mixture is sealed up in a flask and kept at the ordinary temp.; it is at first clear, but has a red colour. In a few minutes a brown precipitate begins to separate, and the reaction is complete in about three hours. The product is filtered through glass wool, washed with carbon disulphide, and dried in vacuo, the apparatus being filled with carbon dioxide until the latter is removed by the pump. The product is **boron phosphodiiodide,** BPI_2, an amorphous, homogeneous, deep-red powder. When heated in a vacuum, it melts at 190°–200°, and will remain in superfusion at the ordinary temp. for a long time; in a vacuum, it begins to volatilize at 170°–200°, and condenses on the cold part of the tube in distinct red crystals. It is only very slightly soluble in carbon bisulphide, and seems to be completely insoluble in benzene, phosphorus trichloride, and carbon tetrachloride. It is extremely hygroscopic, and decomposes very rapidly in moist air. In presence of a large excess of water, it becomes yellow, without apparent development of heat, and hydriodic, phosphorous and boric acids are formed, a small quantity of phosphine being evolved, and a small quantity of a yellow substance with an odour of phosphorus being deposited. With a very small quantity of water, the yellow precipitate is produced in larger quantity, and a distinct quantity of phosphonium iodide is formed. When boron phosphodiiodide is heated in hydrogen sulphide, it yields boron sulphide, phosphorus sulphide, and hydrogen iodide without any free iodine. Dil. nitric acid yields phosphoric acid and boric acid, whilst strong nitric acid produces the same result, but with incandescence. Ordinary or fuming sulphuric acid has no action in the cold, but, on heating, free iodine, hydrogen iodide, and sulphur dioxide are evolved. Phosphorous trichloride and carbon tetrachloride have no action even in sealed tubes at 100°. Chlorine produces incandescence with formation of boron chloride, iodine chloride, and phosphorus pentachloride. When heated in oxygen, the compound burns and yields iodine, boric anhydride, and phosphoric anhydride. Sodium has no action in the cold, but decomposition takes place near the m.p. of the metal. Powdered magnesium reacts with incandescence. When thrown into mercury vapour, the phosphodiiodide takes fire at once. In the presence of carbon bisulphide the behaviour of metals is different; magnesium or sodium at the ordinary temperature produces a red compound, PBI, whilst silver or mercury in the cold, or more rapidly at 100°, yields a maroon-coloured compound with the properties of boron phosphide, BP. When boron phosphodiiodide is heated in an atm. of hydrogen, **boron phosphoiodide,** BPI, is formed as an amorphous, red powder, somewhat less hygroscopic than the diiodide. It volatilizes in a vacuum at 210°–250° without previous fusion, and condenses in orange-yellow crystals. Strong nitric acid decomposes it with development of heat and without incandescence, iodine being liberated. Conc. sulphuric acid has no action in the cold, but, on heating, iodine, sulphurous anhydride, and boric acid are formed. When heated out of contact with air, it decomposes at a temp. below dull redness with evolution of vapour of iodine and boron phosphide. Mercury in excess, in presence of dry carbon disulphide, yields mercuric iodide and boron phosphide at the ordinary temp.

Some unanalyzed aluminium phosphides were obtained by F. Wöhler[13] by burning aluminium in the vapour of phosphorus; but O. Emmerling could not make the phosphorus vapour attack the red-hot aluminium. H. Fonzes-Diacon, and C. Matignon ignited a mixture of red phosphorus and aluminium powder in a crucible and observed a lively reaction. Yellow crystals of phosphide were obtained; and L. Franck obtained needle-like crystals by heating a mixture of aluminium and phosphorus in an atm. of air or hydrogen in a sealed tube at a red-heat. A. Rossel and L. Franck prepared **aluminium pentitatriphosphide,** Al_5P_3, as a grey crystalline mass, by passing the vapour of phosphorus over aluminium at a high temp., and heating the product until phosphorus is no longer evolved. L. Franck obtained **aluminium tritaheptaphosphide,** Al_3P_7, by heating an intimate mixture of aluminium powder and red phosphorus to a white-heat in a current of hydrogen. The grey crystalline mass is pulverulent; it can be heated in air without change; it gives off phosphine when treated with water or dil. acids; and it is decomposed by exposure to moist air, forming aluminium hydroxide, etc. If the mixtures be heated in an electric furnace, L. Franck found that **aluminium tritaphosphide,** Al_3P, and **aluminium monophosphide,** AlP, can be produced. These phosphides have both metallic appearance and crystalline fracture, and give off phosphine when treated with water. L. Losana examined the effect of a little phosphorus on the mechanical properties of aluminium—they are improved by up to 0·1 per cent. additions, but higher proportions reduce the tenacity and elongation.

A. Lamy[14] said that thallium unites directly with phosphorus, but E. Carstanjen found that no **thallium phosphide** is formed either when the two elements are melted together in a closed crucible, or when pieces of phosphorus are projected into molten thallium in an atm. of carbon dioxide. H. Flemming said that phosphorus vapour passed over molten thallium produces a thin layer of a black substance. E. Carstanjen did not obtain thallium by passing hydrogen over molten thallium phosphate; or by heating a mixture of thallium phosphate and carbon. H. Flemming found that phosphorus does not act on the thallium salts, but with aq. soln. of thallous hydroxide, a black deposit of thallium appears; and when phosphorus is heated with a thallous hydroxide soln. in a sealed tube, a little phosphine appears, a black substance is formed and some phosphoric acid passes into soln. W. Crookes said that when phosphine is passed into an ammoniacal soln. of thallous sulphate, a black powder of thallium phosphide is formed which is stable in air. P. Kulisch said that phosphine is without action on neutral and acid soln. of thallous salts, and thallium is precipitated from alkaline soln. Hence only small quantities of the phosphide can be obtained by W. Crookes' process. Only a small quantity of a precipitate was obtained after passing phosphine through the soln. for a day; this precipitate gave off a little phosphine when treated with acids. Thallic salts are incompletely reduced by phosphine to thallous salts.

T. Thomson[15] thought that he had obtained what he called a *carburet of phosphorus*—or carbon phosphide—when impure calcium phosphide is decomposed by water, and the lime removed by hydrochloric acid: the residual carbon phosphide was collected on a filter and quickly washed. It was said to be a brownish-yellow, soft, tasteless, inodorous, infusible powder, which suffers no alteration in dry air below 100°, but takes fire at a red-heat when the phosphorus burns to phosphoric acid while the carbon is not changed. It attacks moisture from the air, forming a hydrocarbon, and carbon dioxide. The properties of the alleged phosphide correspond with those of a mixture of carbon and phosphoric acid with perhaps a small proportion of phosphorus. J. J. Berzelius said that a similar substance remains when crude phosphorus is pressed through chamois leather. J. B. Trommsdorff obtained what he regarded as *Phosphorkohlenoxydgas*, or *hydrogen carbophosphide* which existed in the gaseous state at ordinary temp. during the distillation of phosphoric acid with charcoal. T. de Grotthus said that *phosphorcarburetted hydrogen gas* is obtained by dissolving phosphorus in an alcoholic soln. of potassium hydroxide. There is nothing to show that the gaseous product is any different from a mixture of hydrogen, carbon monoxide, and a little phosphorus vapour. A. Bor attempted unsuccessfully to effect *la combinaison du phosphore du carbone.*

J. J. Berzelius[16] said that red-hot silicon does not take up phosphorus vapour; and O. P. Watts was unable to prepare a **silicon phosphide** by reducing phosphoric acid with carbon and silicon in an electric furnace, or by using copper or copper silicide as a flux, or by the action of phosphor tin on silicon. J. Gewecke, however, said that silicon tetrachloride reacts with phosphine, forming silicon phosphide. According to R. Chenevix, a white, brittle, granular **titanium phosphide** is produced when titanium phosphate mixed with charcoal and a little borax is strongly ignited. H. Rose also obtained the phosphide; and F. Wöhler said the phosphide is not obtained by heating a mixture of titanic oxide, phosphoric acid, and carbon in a graphite crucible over 1400°, but it can be prepared by passing titanium phosphinochloride vapour mixed with phosphine through a red-hot glass tube when a layer of grey titanium phosphide appears on the glass. H. Moissan also found that at 1000°, phosphorus vapour covers titanium with a film of a dark-coloured phosphide. J. Gewecke investigated F. Wöhler's reaction, and found that when titanium tetrachloride is treated in the cold with phosphine, it forms a yellow crystalline substance which when heated decomposes into phosphine, hydrogen chloride, and a little titanium phosphide, TiP, which appears in the form of a brittle mass with a metallic lustre, and sp. gr. 3·95 at 25°/4°. A. E. van Arkel and J. H. de Boer made titanium phosphide by passing the vapour of the metal chloride and phosphorus over a heated tungsten filament; and F. P. Venable and R. O. Dietz, by passing the phosphine over the heated chloride. R. Chenevix said that the phosphide did not melt before the blowpipe, and seemed not very fusible. According to H. Moissan, the phosphide is a conductor of electricity, and burns when heated in air, or when fused with potassium nitrate. It is insoluble in dil. or conc. acids or alkali-lye; and is oxidized only to a small extent when boiled with aqua regia, or when heated with fuming nitric acid at 250°–300°. When heated in chlorine, the phosphide burns, forming white fumes of titanium tetrachloride and phosphorus pentachloride which condense as a complex titanium phosphoenneachloride, $TiPCl_9$. According to J. Gewecke, when zirconium tetrachloride is treated with phosphine, it behaves as in the case of titanium tetrachloride, yielding **zirconium diphosphide**, ZrP_2, which resembles titanium monophosphide in its general chemical and physical properties. The glistening grey mass has a sp. gr. of 4·77 at 25°/4°. When zirconium tetrachloride is sublimed in a current of hydrogen over heated potassium phosphide, there is formed a black mass containing potassium chloride, zirconium, phosphorus, and possibly oxygen derived from the presence of some zirconium oxychloride. A. E. van Arkel and J. H. de Boer made zirconium phosphide, and also **hafnium phosphide**, by the process used for titanium phosphide. J. J. Berzelius[17] noticed that when thorium is heated with phosphorus, the two elements unite with incandescence. J. Gewecke could not prepare **thorium phosphide** by the action of phosphine on thorium tetrachloride, even at a high temp., although H. Moissan and H. Martinsen obtained the phosphide by heating thorium tetrachloride to redness in a stream of phosphorus vapour; A. E. van Arkel and J. H. de Boer made thorium phosphide by the process used for titanium phosphide.

Experiments on the formation of **tin phosphides** were made by B. Pelletier,[18] O. Emmerling, C. Künzel, R. Lüpke, etc., who obtained a silvery-white alloy with 13–14 per cent. of phosphorus by heating the two elements together. Indefinite tin phosphides were made by A. Schrötter, and P. Vigier, who passed phosphorus vapour over the heated metal. G. Landgrebe melted tin with fused microcosmic salt; P. Berthier heated tin dioxide, tin, carbon, bone-ash, powdered quartz and borax; P. Mellmann, and J. L. Seyboth, heated phosphatic materials sand, tin or stannic oxide, and carbon; S. Natanson and G. Vortmann, metaphosphoric acid, carbon, and tin; A. Granger, by the action of phosphorus trichloride on tin at 500°; and T. von Grotthus, by the action of phosphine on tin salts. Commercial *phosphor-tin* contains 10 per cent. or more phosphorus, and is used extensively in making phosphor-bronze. The applications of phosphor-tin were discussed by F. von Friese, P. F. Nursey, W. G. Otto, etc. Phosphor-tin is very brittle and has a very pronounced crystalline fracture; a polished surface, etched by immersion in dil. nitric acid (0·5 per cent.), shows under the microscopic plate-like crystals immersed in a matrix of tin. The crystals can be obtained in the form of hexagonal plates by the action of dil. nitric acid or of mercury in which they are insoluble; the mercury can be removed by heating the crystals to 400° in a stream of carbon dioxide. L. Losana said that a small proportion of phosphorus has a deleterious effect on the mechanical properties of tin.

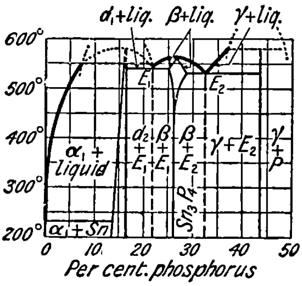

FIG. 23.—Equilibrium Diagram of the Binary System: Sn–P.

P. Jolibois considers that only tin triphosphide and tritetritaphosphide are chemical individuals; and that the other phosphides which have been reported are solid soln. or mixtures. A. C. Vivian found that when a mixture of phosphorus and tin is heated in sealed tubes, two conjugate soln. appear to be formed, and two definite layers of molten liquid are present. The maximum amount of phosphorus alloying with tin is 8 per cent., and the product melts at about 485°; if phosphorus vapour be absent, about 2·5 per cent. of phosphorus is retained by the tin at about 485°. The first approximation to the equilibrium diagram is shown in Fig. 23, where E_1 and E_2 represent the two eutectics; and Greek letters, solid soln. There is evidence of the formation of tin triphosphide, SnP_3, a compound prepared by P. Jolibois. This phosphide commences to dissociate at about 480°. There is also evidence of the formation of tin tritetritaphosphide, Sn_4P_3, isolated by J. E. Stead. The composition of the crystals from an alloy with 0·4 per cent. of phosphorus corresponds, according to J. E. Stead, with **tin ditritaphosphide,** Sn_3P_2; and, according to M. Ragg, the crystals obtained from a 5 per cent. alloy, correspond with **tin hemiphosphide,** Sn_2P. W. Gemmell and S. L. Archbutt found that phosphor-tin with 5 per cent. of phosphorus is vigorously attacked by aqua regia giving off phosphine; the action is less vigorous with nitric acid of sp. gr. 1·2, and no phosphine is given off. P. Jolibois found that alloys of tin with up to 13 per cent. of phosphorus contain **tin tritetritaphosphide,** Sn_4P_3, which can be isolated by making one of these alloys the positive pole in a soln. of sodium polysulphide—the uncombined tin dissolves, the silver-white crystals of the tritetritaphosphide remain unchanged. This phosphide has a sp. gr. 5·1810, and begins to dissociate at 480°. It is oxidized by nitric acid, and decomposed by hydrochloric acid and by sodium hydroxide. Alloys with more than 13 per cent. of phosphorus can be obtained by heating the mixtures under press., and when these alloys are treated first with hydrochloric acid, then with warm soda-lye, and finally with nitric acid at 50°, the monophosphide is obtained. A. Schrötter, S. Natanson and G. Vortmann, and O. Emmerling prepared crystals corresponding with the monophosphide by heating finely-divided tin with phosphorus vapour to a dull red heat; and S. Natanson and G. Vortmann prepared the same compound by heating a mixture of metaphosphoric acid with carbon and tin. The monophosphide has a sp. gr. of 6·56; it is soluble in hydrochloric acid; and not attacked by ordinary nitric acid, but it is attacked by the fuming acid; and, according to P. Jolibois, it dissociates when heated to 415°, forming the tritetritaphosphide. When tin is heated with a great excess of phosphorus in an evacuated tube,

A. Schrötter, and O. Emmerling found evidence of the existence of **tin diphosphide,** SnP_2, of sp. gr. 4·91; this substance is not attacked by hydrochloric acid, but aqua regia decomposes it with a series of explosions and the development of phosphine. P. Jolibois obtained **tin triphosphide,** SnP_3, by heating a mixture of tin and red phosphorus in a sealed tube for 10 hrs. at 620°. The product contained 40 per cent. of phosphorus, and it was purified by treatment with hydrochloric acid, followed by a hot dil. soda-lye, and by nitric acid of sp. gr. 1·2 at 50° and diluted with an equal vol. of water. The crystals have the appearance of elemental silicon. The sp. gr. is 4·10 at 0°; it dissociates into phosphorus and the tetratritaphosphide at 415°; it is insoluble in hydrochloric acid; slowly attacked by dil. nitric acid; and reacts with incandescence with fuming nitric acid. H. Rose reported **tin pentaphosphide,** SnP_5, to be formed as a yellow powder by the action of water on tin phosphinotetrachloride. L. C. Glaser and H. J. Seemann studied the system: Cu–Sn–P.

According to B. Pelletier,[19] molten lead can take up about 1·5 per cent. of phosphorus; and a similar alloy is obtained when lead filings are heated with glacial phosphoric acid, or when phosphorus is heated with lead chloride. A. Stock and F. Gomolka, and A. C. Vournasos obtained a phosphide by projecting pieces of molten phosphorus on molten lead. It contained needle-like crystals of lead and phosphorus in the molar proportion 3 : 7—possibly *lead diphosphide*, PbP_2. G. Linck and P. Möller said the crystals are monoclinic with the axial ratios $a:b:c = 1·651:1:1·46$, and $\beta=72° 40'$; the sp. gr. is greater than 3·2; and the crystals are less soluble than lead in nitric acid. A. C. Vournasos obtained a similar product by melting lead and phosphorus together under paraffin. P. S. Braucher used an alloy with 0·25 per cent. of phosphorus. P. Hautefeuille and A. Perrey said that lead heated in phosphorus vapour below the m.p. absorbs only a little phosphorus, and the phosphorus dissolved by molten lead is rejected on solidification. A. Granger could not get phosphorus and lead to unite directly, nor indirectly by the action of phosphorus on lead chloride or oxide, and he considered *l'existence de ces phosphures est donc douteuse.* T. von Grotthus, and H. Rose obtained a brown precipitate by passing phosphine into a soln. of lead acetate. P. Kulisch said that acid soln. of lead salts give no precipitate when treated with phosphine; a black precipitate is readily obtained by passing phosphine into lead acetate dissolved in a soln. of potassium hydroxide or aq. ammonia; A. Brukl worked with an alcoholic soln. of potassium hydroxide and obtained a precipitate of normal **lead phosphide,** Pb_3P_2. The precipitate is so unstable that it is liable to decompose, leaving a film of lead on the glass walls of the containing vessel. Water and alkali-lye decompose it slowly, forming lead, phosphine, and phosphoric acid. Dil. acids give phosphine; conc. nitric acid partially oxidizes the phosphide. R. Bossuet and L. Hackspill treated a soln. of lead nitrate with rubidium dipentitaphosphide in the same menstruum, and obtained black, amorphous **lead pentaphosphide,** PbP_5. It spontaneously inflames in air; and at 400°, in vacuo, it gives off much phosphorus; water attacks it slowly; nitric acid gives lead nitrate and phosphoric acid; and dil. sulphuric acid and hydrochloric acid form solid hydrogen phosphide, and lead sulphate or chloride respectively.

H. Rose [20] prepared **chromium monophosphide,** CrP, by passing phosphine over heated chromic chloride; C. A. Martius, by the action of phosphorus vapour on potassium dichromate; and J. J. Berzelius, by heating a mixture of charcoal and chromic phosphate in a graphite crucible. The monophosphide was made by A. Granger by heating phosphorus with chromium or chromic chloride in a glass tube in an atm. of nitrogen at 900°. G. Maronneau also made a chromium phosphide by heating copper phosphide with chromium filings in an electric furnace. The phosphide is a dark grey crystalline powder of sp. gr. 4·68–5·71. J. J. Berzelius found that it fuses with difficulty, and conducts electricity. The phosphide is decomposed by potash-lye, or molten potassium hydroxide; it is insoluble in acids, but it is very slightly attacked by aqua regia, and dissolved a mixture of hydrofluoric and nitric acids.

B. Pelletier[21] reported a **molybdenum phosphide** to be formed by the action of phosphorus vapour on molybdenum, but he did not examine the product further. F. Wöhler represented its formula by MoP, and obtained it by heating a mixture of molybdenum trioxide, and phosphoric acid, in a carbon crucible above 1400° for some hours; and washing the product with hydrochloric acid and soda-lye. The grey, crystalline powder has a sp. gr. 6·167; it fuses with great difficulty; and conducts electricity. In a soln. of cupric sulphate containing zinc and hydrochlroic acid, the phosphide acquires a coating of copper. It slowly oxidizes without burning when heated in air. It also forms molybdenum and phosphorus chlorides when heated in chlorine; hot nitric acid converts it into molybdic and phosphoric acids; and molten potassium nitrate oxidizes it with incandescence. B. Pelletier made the qualitative observation that tungsten heated with phosphorus vapour forms a phosphide, and F. Wöhler represented it as **tungsten hemiphosphide,** W_4P_2, and made it by heating a mixture of tungsten trioxide, and phosphoric acid in a carbon crucible for some hours above 1400°. The lustrous, dark, steel-grey mass contained six-sided prisms of sp. gr. 5·207. The phosphide conducts electricity; it does not change when heated to a high temp.; and oxidizes very slowly when heated to redness in air. It burns when heated on charcoal in oxygen; and with *einem blendenden Glanz* when added to fused potassium chlorate. It is not attacked by any known acid, not even by aqua regia; it is opened up by a fused mixture of potassium carbonate and nitrate; and it behaves like molybdenum phosphide towards a soln. of copper sulphate. According to E. Defacqz, when tungsten diphosphide is heated with copper in the electric furnace, it is decomposed; but if it is heated with a large excess of copper phosphide in a graphite crucible in a wind furnace and the product treated with dil. nitric acid, a new phosphide, **tungsten monophosphide**, WP, is obtained in grey, lustrous, prismatic crystals of sp. gr. 8·5. This compound burns in air or oxygen at a red-heat, and is likewise attacked by chlorine, but it is not decomposed by hydrofluoric or hydrochloric acid, or by hydrogen chloride. It is slowly oxidized by hot nitric acid, and is rapidly dissolved by a mixture of nitric and hydrofluoric acids, or by aqua regia. Sodium and potassium hydroxide soln. have no action on the phosphide, but the fused hydroxides and fused mixtures of alkali carbonates and nitrates readily oxidize it, whilst fused potassium hydrosulphate attacks it slowly. He also prepared tungsten diphosphide, WP_2, by heating tungsten hexachloride at 450° in a current of hydrogen phosphide. This compound is a black, crystalline mass, insoluble in water and the ordinary organic solvents, and having a sp. gr. 5·8. Fluorine attacks the diphosphide at temp. above 100°, forming phosphorous and tungsten fluorides; chlorine and bromine react similarly at a red-heat; when liquid chlorine is employed at 60°, a chlorophosphide is produced. Sulphur and nitrogen both displace the phosphorus from this compound at high temp., forming the disulphide and nitride respectively; the disulphide is also produced by the action of hydrogen sulphide on the phosphide at 500°. The diphosphide readily burns in air or oxygen, forming tungstic and phosphoric oxides, its combustion in the latter gas being attended by a very dazzling flame. A complete reduction of the phosphide is effected by heating it with copper or zinc, tungsten being liberated, and the corresponding metallic phosphide produced; the reduction by hydrogen commences at 525°, but is incomplete even at 900°. Lead at 900° only partially reduces the diphosphide, and copper phosphide at 1400° produces another tungsten phosphide; when heated with iron, the diphosphide is converted into a double **iron tungsten phosphide**; with aluminium, the reaction is even more complicated, and the product contains a large amount of silicon derived from the crucible. Hydrofluoric and hydrochloric acids do not act on the diphosphide, but a mixture of the former with nitric acid dissolves this compound even in the cold, whilst aqua regia decomposes it on warming; sulphuric and nitirc acids, when heated, are reduced by the phosphide, sulphurous acid and blue tungsten oxide being formed in the first case, and nitrous and tungstic acids in the second. The diphosphide is dissolved by fused caustic alkalies and potassium hydrogen sulphate, and is even more readily attacked by heating mixtures of alkali nitrates and carbonates.

The properties of **nitrogen phosphide** are discussed in connection with phosphorus nitride. G. Landgrebe[22] prepared *Phosphorarsen* by heating a mixture of phosphorus and arsenic to dull redness, but J. V. Janowsky regarded the product as a mixture, and he said the same thing about the product of the action of phosphorus vapour on heated arsenic; and the action of sodium or calcium arsenide on phosphorus trichloride. According to C. E. E. Ritter, and N. Blondlot, **arsenic hemiphosphide,** As_2P, is formed slowly when phosphorus is allowed to remain in contact with an aq. soln. of arsenious or arsenic acids, and rapidly if the soln. be acidified with hydrochloric acid. The unchanged phosphorus can be removed by treatment with carbon disulphide. The black mass becomes brown when exposed to air, and it forms arsenic trioxide when kept under water. J. V. Janowsky obtained **arsenic monophosphide,** by the action of dried arsine on phosphorus trichloride below 20°, because at higher temp. some of the arsenic forms a volatile chloride. The excess of trichloride is separated, and the product dried in a current of carbon dioxide at 70°–80°; J. V. Janowsky made it by the action of phosphine on arsenic chloride—A. Cavazzi used a hydrochloric acid soln. of arsenic trioxide. A. Besson found that phosphine begins to react similarly with arsenic trifluoride at —23°; with arsenic trichloride at —18°; while solid arsenic tribromide or triiodide is only superficially attacked, and the tribromide reacts vigorously with phosphine at 20°. If the product of these reactions is washed with water, J. V. Janowsky said that an oxyphosphide is formed, and A. Besson, that impure arsenic phosphite and phosphate are produced. According to J. V. Janowsky, arsenic monophosphide is a reddish powder which burns when heated in air to arsenic trioxide and phosphorus pentoxide; but if heated out of contact with air, or in a current of carbon dioxide, phosphorus first sublimes and then arsenic. Sulphuric and hydrochloric acids dissolve the phosphide only when heated therewith; conc. nitric acid oxidizes it with incandescence, and the dil. acid dissolves it, forming, when heated, arsenic and phosphoric acids; chlorine, bromine, and iodine form the corresponding trihalides of arsenic and phosphorus; potash-lye, aq. ammonia, and baryta-water decompose the phosphide at ordinary temp., and rapidly when heated, forming phosphine, arsine, arsenic, phosphorous acid, and arsenic trioxide. It is slightly soluble in carbon disulphide, but not in alcohol, ether, or chloroform.

According to J. V. Janowsky, if freshly precipitated arsenic phosphide be treated with water, it forms *arsenic dioxydiphosphide*, $As_3P_2O_2$, which decomposes slowly at 100°, and rapidly at 200°. It is not attacked by the ordinary acids other than nitric acid; and it is attacked by alkali-lye, chlorine, bromine, and iodine as in the case of the monophosphide. As indicated above, A. Besson does not agree with J. V. Janowsky on the action of water on arsenic monophosphide. O. Ruff reported *arsenic dioxyphosphide*, As_4PO_2, to be formed by adding red phosphorus to arsenic trichloride containing some aluminium chloride; the red product when treated with water yields the violet-black oxyphosphide.

B. Pelletier[23] obtained an antimony phosphide by the action of molten antimony on metaphosphoric acid with or without admixed carbon. B. Pelletier, and G. Landgrebe obtained a phosphide by the action of phosphorus on molten antimony, although W. Ramsay and R. W. E. McIvor could obtain a product with only 15·46 per cent. by direct action. The last-named prepared **antimony monophosphide,** SbP, by the action of phosphorus on a soln. of antimony tribromide in carbon disulphide. M. Ragg could not prepare the monophosphide by this process, nor by the action of phosphine on tartar emetic, or antimony trichloride. The phosphide prepared by the fusion processes is a brittle, white mass with a crystalline fracture; the precipitated product is a red powder insoluble in carbon disulphide, ether, and benzene. O. Ruff found that phosphorus reacts with antimony chloride in the presence of aluminium chloride—*vide supra*, arsenic oxyphosphide.

B. Pelletier,[24] and C. M. Marx found that molten bismuth dissolves a little phosphorus, and W. Heintz, that when bismuth phosphate is heated in a current of hydrogen, the product may contain some **bismuth phosphide,** but the properties of both products resemble those of a phosphiferous bismuth. J. J. Berzelius, T. von Grotthus, and G. Landgrebe precipitated a black bismuth phosphide by phosphine from a soln. of bismuth nitrate as nearly neutral as possible. The liberated nitric acid decomposes the phosphine so that the yield is small. A. Cavazzi passed phosphine into a soln. of bismuth trichloride with as little free acid as possible, but obtained a black precipitate consisting of bismuth and phosphorus mixed with some oxide and chloride. P. Kulisch said the precipitate may be a mixture of bismuth phosphide and oxychloride, and he obtained no precipitate with a soln. containing 20 grms. of bismuth trioxide in 100 c.c. of hydrochloric acid of sp. gr. 1·124. A. Cavazzi said that when phosphine acts on dry bismuth chloride at 100°, hydrogen chloride is evolved and what is considered to be a bismuth phosphide remains. If phosphine is passed into an ethereal soln. of bismuth trichloride, A. Cavazzi and D. Tivoli observed the formation of a black, hygroscopic deposit with the composition PBi_3Br_7, and considered to be *hydrotrisdibromobismuthphosphonium bromide*, $P(BiBr_2)_3HBr$. When the impure phosphide is heated in a current of carbon dioxide, some phosphorus is volatilized; when heated in air, phosphorus burns with its characteristic flame leaving a white residue of variable composition; when boiled with water, bismuth separates partly as metal, and most of the phosphorus passes into phosphoric acid and a little phosphine; dil. nitric acid freely dissolves the phosphide; dil. sulphuric and hydrochloric acids are without action; conc. hydrochloric acid decomposes it at ordinary temp. with the evolution of non-spontaneously inflammable phosphine; boiling conc. sulphuric acid forms phosphine and sulphur dioxide; and with boiling alkali-lye, bismuth is deposited, and hydrogen, with a little phosphine, evolved.

J. J. Berzelius[25] said that when vanadyl phosphate, mixed with some sugar, is heated, the grey, porous mass which is formed can be pressed together when it has the appearance and lustre of graphite. It is considered to be an impure **vanadium phosphide.**

B. Pelletier[26] prepared a white manganese phosphide by heating manganese with microcosmic salt, and charcoal, or by passing phosphorus vapour over manganese; and H. Rose, J. Percy, and F. Wöhler made a similar alloy by heating calcined pyrolusite with bone-ash, sand, and charcoal. H. Struve prepared what appeared to be a mixture of phosphides by reducing manganese pyrophosphate with carbon; C. Matignon and R. Trannoy obtained a metal rich in phosphides by reducing manganese phosphate by the aluminothermite process; E. Wedekind and T. Veit said that the crystalline product obtained by the thermite process from manganese and red phosphorus is a mixture which is readily attacked by water and dil. acids, and has only feeble magnetic qualities. H. von Jüptner also prepared manganese and manganese phosphide alloys. S. F. Schemtschuschny and N. N. Efremoff determined the f.p. of alloys of manganese with up to 47 per cent. of phosphorus. The alloys were made by melting the metal in a fireclay crucible under fused barium chloride, and adding the phosphorus through a tube made of asbestos. The phosphorus vapour was slowly absorbed by the molten metal. More conc. alloys gave off phosphorus vapour when the attempt was made to work with them. The results are shown in Fig. 24. The two maxima—one at approximately 1390°, and the other at 1190°—correspond with the compounds Mn_5P_2 and MnP; the corresponding eutectics were at 964° and 1095°. Alloys with less than 10 at. per cent. of phosphorus are not magnetic, but with over this quantity the magnetizability rises with increasing proportions of phosphorus up to the appearance of the dipentitaphosphide; after that, the magnetizability becomes perceptibly feebler.

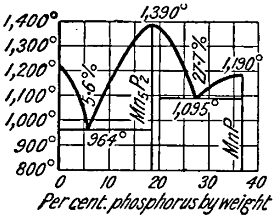

FIG. 24.—Freezing-point Curve of Manganese and Phosphorus.

A. Schrötter prepared an alloy with a composition approximating **manganese tritaphosphide,** Mn_3P, by heating manganese in the vapour of phosphorus at a very dull red-heat; union occurs with incandescence. The sp. gr. of the product is 4·94; it is insoluble in hydrochloric acid, and freely soluble in nitric acid. E. Wedekind and T. Veit prepared **manganese dipentitaphosphide,** Mn_5P_2, when manganese chloride and phosphorus are heated to redness in a current of hydrogen. The conditions of stability are indicated in Fig. 24. It has moderately strong magnetic properties. S. F. Schemtschuschny and N. N. Efremoff gave 1390° for the m.p.; and E. Wedekind and T. Veit reported that the dipentitaphosphide is a dark grey crystalline powder which is stable towards hydrochloric acid or boiling water, but dissolves freely in hot nitric acid. A. Granger reported **manganese ditritaphosphide,** Mn_3P_2, to be formed by heating manganese chloride with phosphorus in an atm. of hydrogen in a sealed tube. The product was washed with water, and small, strongly refracting needles resembling manganite were obtained. E. Wedekind and T. Veit also obtained glistening needles of this phosphide by heating a mixture of manganese and red phosphorus in a current of hydrogen, and finally over the oxyhydrogen flame. They gave 5·12 for the sp. gr. at 18°, and found that it has strong magnetic properties, and when compact is a good electrical conductor. They also said that it dissolves in hot conc. nitric acid, but it is stable towards dil. acids. A. Granger reported that his product was attacked by aqua regia, but not by nitric acid. The phosphide oxidizes slowly when heated in air or oxygen; and it inflames when gently heated in chlorine.

S. Hilpert and T. Dieckmann made **manganese monophosphide,** MnP, by heating the two elements in an evacuated sealed tube at 600° for 10–12 hrs., and then washing the product with 10 per cent. hydrochloric acid. The conditions of stability are indicated in Fig. 24. S. F. Schemtschuschny and N. N. Efremoff gave 1190° for the m.p.; and S. Hilpert and T. Dieckmann found that the monophosphide is an inodorous, black powder of sp. gr. 5·39 at 21°/4°, which burns on heating in air, giving black oxidation products; it is insoluble in hydrochloric acid, but readily soluble in nitric acid. The magnetic properties are lost at 18° on heating, and regained at 26° on cooling. S. Hilpert and T. Dieckmann prepared **manganese diphosphide,** MnP_2. A mixture of manganese (2 grms.) and red phosphorus (2·4 grms.) was heated in an exhausted and sealed Jena-glass tube, first at 400°, and finally at 600°, for a considerable length of time. Any phosphorus unacted on is distilled into the drawn-out end of the tube. The grey contents of the tube, after triturating with benzene, and washing with alcohol and ether, were dried over sulphuric acid in vacuo; they suffered no alteration in weight after heating for 13 hrs. in a current of hydrogen at 290°. When heated at 400°, however, phosphorus was gradually lost, giving, finally, the monophosphide.

The **phosphides of iron** and of copper have been more closely investigated than those of any other element, no doubt because of their industrial importance. About 1780, T. Bergman,[27] and J. K. F. Meyer found iron phosphide in commercial iron, and they regarded it as a peculiar, elemental metal which they designated *siderum*, *Wassereisen*, or *hydrosiderum*; and it was afterwards recognized as a compound of iron and phosphorus by J. K. F. Meyer, M. H. Klaproth, L. N. Vauquelin, and C. W. Scheele. J. K. F. Meyer commenting on his mistake said: To err in chemistry is alas too easy (*Das Irren ist in der Chemie doch, leider! gar zu leicht*). The impure phosphide was made by C. Hatchett by passing the vapour of phosphorus over red-hot iron filings, or by projecting pieces of phosphorus on them; B. Pelletier, by igniting iron filings mixed with phosphoric acid—with or without carbon; F. Wöhler, by heating a mixture of iron filings, bone-ash, quartz-sand, and carbon; J. J. Berzelius, by igniting a mixture of ferrous phosphate and lamp-black—if too much carbon is used, an iron carbide is formed which can be dissolved out by hydrochloric acid with the loss of half the phosphide; and H. Rose, by passing phosphine over gently heated iron pyrites. T. Swann heated iron scrap and phosphate rock in the electric furnace; and E. V. Rawn heated a low-grade ferrophosphorus with a material containing phosphorus, and a flux in an electric furnace.

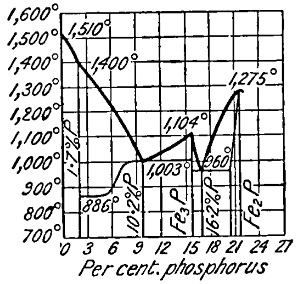

FIG. 25. — Freezing-point Curves of the Fe–P System (B. Sakalatwalla).

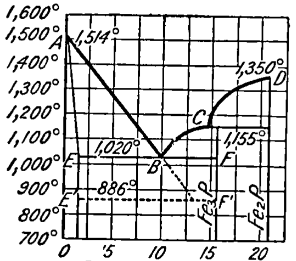

FIG. 26. — Freezing-point Curves of the Fe–P System (N. S. Konstantinoff).

Phosphides ranging from Fe : P=2 : 3 to 6 : 1 have been reported; but, on the f.p. curve for alloys with less than 25 per cent. of phosphorus, only the trita- and hemi-phosphides have been observed. The f.p. curve of a portion of the Fe–P system has been studied by E. Gercke, J. E. Stead, N. S. Konstantinoff, and B. Sakalatwalla. According to J. E. Stead, the alloys of phosphorus and iron can be divided into five classes: (i) those containing 0–1·7 per cent. of phosphorus and consisting of solid soln. of Fe_3P in iron; (ii) alloys with 1·7–10·2 per cent. of phosphorus, which form solid soln. of Fe_3P in iron and give a eutectic alloy (10·2 per cent. P) consisting of a definite solid soln. and the phosphide Fe_3P; (iii) those with 10·2–15·58 per cent. P, also consisting of the eutectic and Fe_3P, the m.p. of the latter (15·58 per cent. P) being 1060°; (iv) alloys containing 15·58–21·6 per cent. P and consisting of Fe_3P and Fe_2P; (v) those with more than 21·6 per cent. P and containing Fe_2P and another phosphide richer in phosphorus. The results of B. Sakalatwalla are illustrated by Fig. 25. The m.p. of iron is lowered from 1510° to about 1400° by the addition of 1·7 per cent. of phosphorus; by increasing the proportion of phosphorus to 10·2 per cent. the f.p. curve shows two arrests. The second one refers to the eutectic line which commences at about 886°, and rises to about 1003° as shown in the diagram. This unusual behaviour is attributed to the existence of a definite phosphide with between 6·5 and 8 per cent. of phosphorus, so that the corresponding eutectic has a different composition to that with 10·2 per cent. of phosphorus. The f.p. with increasing proportions of phosphorus rises from the eutectic to a maximum at about 1104° corresponding with the tritaphosphide; the f.p. curve then falls to a second eutectic about 960° with about 16·2 per cent. of phosphorus. The f.p. curve then rises to about 1275° corresponding with the hemiphosphide. Only one sample was examined with over this amount of phosphorus, and the alloy with 24·5 per cent. of phosphorus had arrests at 1295° and 1218°. Alloys with up to 1·7 per cent. of phosphorus are solid soln. of phosphorus in iron. N. S. Konstantinoff interprets his results rather differently as illustrated by Fig. 26. Here, the f.p. curve for alloys with up to 21 per cent. of phosphorus has three branches: (i) *AB*, falling from 1514°, the m.p. of iron, to 1020°, corresponding with 10·2 per cent. Fe; (ii) *BC*, rising continuously from *B* to *C*, and corresponding with the separation of crystals of the phosphide Fe_3P. The separate solidification curves exhibit two halts, one showing a regular rise corresponding with the separation of crystals of the phosphide, and the other at a constant temperature corresponding with separation of the eutectic and gradually diminishing in magnitude as *C* is approached. Micrographic examination of these alloys shows the presence of rhomboidal plates of Fe_3P surrounded by the eutectic; (iii) *CD*, rising at first rapidly and afterwards more slowly to the point *D*, corresponding with the phosphide Fe_2P. The second eutectic line alluded to by B. Sakalatwalla is shown by the dotted line *E'F'*. J. L. Haughton also found that the first eutectic at 1050° with nearly 10·5 per cent. phosphorus, consists of the α-solid soln. of phosphorus in iron, and the tritaphosphide. After this, the liquidus curve rises to 1166°, at which temp. the tritaphosphide is formed by a peritectic reaction between the liquid and the hemiphosphide, the latter corresponding with a maximum on the liquidus at 1380°. Beyond this point, the liquidus falls to a second eutectic, the constituents of which are the hemiphosphide and an unknown compound. The tritaphosphide forms no solid soln., but magnetic analysis shows that it undergoes a transformation at about 420°, which is similar to the corresponding transformation in cementite. The compound hemiphosphide forms no solid soln. with an excess of iron, but there may be a very slight range of solid solubility on the phosphorus side. The effect of phosphorus on the critical points is very marked. The A_4 point is rapidly depressed and the A_3 point raised, the two joining to form a completely enclosed area representing the existence of γ-iron. There is thus no boundary between α- and δ-iron, both of which form the same space lattice. H. Junglbluth and H. Gummert studied the effect of annealing on the development of the iron phosphide eutectic.

The microscopic structure of these alloys was also examined by these investigators, J. O. Arnold, J. E. Stead, N. S. Konstantinoff, E. Piwowarsky, and B. Sakalatwalla. The last-named found the hardness on Mohs' scale rose from that of pure iron, 3·5, to between 5 and 5·5 with the smallest addition of phosphorus. The hardness remained constant till in the neighbourhood of the first eutectic, Fig. 25, it rose to 6 with a sample containing 9·93 per cent. of phosphorus, and remained constant up to the first maximum; on passing the second eutectic the hardness rose to 6·5 with a sample containing 16·1 per cent. of phosphorus. The hardness was thereafter lowered with an increasing proportion of phosphorus. The greater hardness of samples with eutectic proportions of the constituents is attributed to the closer grain of the fine eutectic structure as contrasted with the large, homogeneous, crystalline faces presented by the individual components of the non-eutectics. E. d'Amico also studied the hardness of these alloys. C. J. B. Karsten reported that the tenacity of iron is not sensibly affected by the presence of up to 0·3 per cent. of phosphorus, although the metal is a little harder. Iron with 0·6 per cent. of phosphorus will not stand the breaking test, but it can be bent at right angles without breaking; with 0·66 per cent. of phosphorus, the qualities of the iron are not those characteristic of cold-short iron properly so called. The tenacity is notably reduced with 0·75 per cent. of phosphorus, and with 0·8 per cent. the iron is decidedly cold-short; and with 1·0 per cent., a bar cannot be bent at right angles. All iron with over one per cent. of phosphorus is brittle. E. d'Amico found the elastic limit of steel with 0·125 per cent. of carbon was raised about 27 kgrms. per sq. mm. by the addition of each 0·1 per cent. of phosphorus; the tensile strength was raised by 0·5 per cent. of phosphorus, but fell off with higher proportions. The elongation and contraction followed the tensile strength, falling off as the phosphorus rose, and becoming nil with higher proportions. H. M. Howe, A. Ledebur, T. D. West, and J. E. Stead also studied the effect of phosphorus in the presence of varying amounts of carbon on the tensile strength of iron and steel. E. d'Amico found the electrical resistance of phosphorized iron and steel increased as the proportion of phosphorus increased; but the magnetic qualities were influenced by phosphorus only in so far as its presence makes mechanical and thermal treatment impossible. R. Kremann and O. Baukovac studied the electrolysis of iron phosphides.

Several of the phosphides which have been reported are of doubtful individuality. They have been formed in most cases by the direct union of phosphorus and iron. At a dull red-heat, the monophosphide is formed; at a bright red-heat, the hemiphosphide; and at a white-heat, iron retains only a moiety of phosphorus. J. Percy described square prismatic crystals of *iron hexitaphosphide*, Fe_6P, said to be formed by the action of phosphorus on iron at a red-heat. The product was in all probability a mixture of iron and the tritaphosphide. T. Sidot reported *iron tetritaphosphide*, Fe_4P, to be formed by passing the vapour of phosphorus over iron, and afterwards, with the intention of volatilizing the excess of phosphorus, calcined the product in an ordinary crucible. On breaking the fused and cooled mass, the interior was found to be studded with beautiful crystals, many of which were nearly a centimetre in length. The crystals were right prisms with a square base; generally iridescent upon the surface; they were strongly magnetic, and possessed a hardness comparable to that of steel. He suggested that the crystals are isomorphous with rhabdite—*vide infra*—and consequently T. Sidot's product was probably a mixture of iron and the tritaphosphide. H. H. Hvoslef, and H. le Chatelier and S. Wologdine, prepared **iron tritaphosphide,** Fe_3P, by melting the elements together. The iron phosphide can be separated from the cold pulverized product by means of a magnet or by melting copper phosphide with the necessary amount of iron when the tritaphosphide rises to the surface as a separate phase. E. Mallard observed tetragonal crystals of an iron phosphide, approximating FeP(As), were formed by combustion in the coal mines of Commentary, France. The conditions of stability are indicated in Figs. 25 and 26, where, according to B. Sakalatwalla, the m.p. is 1104°, and, according to N. S. Konstantinoff, the m.p. is 1155°; but J. L. Haughton found that the tritaphosphide is formed by a peritectic reaction at about 1166°. H. le Chatelier and S. Wologdine gave 1100° for the m.p., and 6·74 for the sp. gr. L. J. Spencer found that the axial ratio of the tetragonal crystals is $a:c=1:0·3469$. The magnetic transformation point is 445°–435° —*vide supra*. This phosphide dissolves in hydrochloric acid with the production of hydrogen: $2Fe_3P+12HCl+8H_2O=6FeCl_2+2H_3PO_4+11H_2$. O. Kuhn reported **iron dipentitaphosphide,** Fe_5P_2, to be formed by melting together a mixture of bone-ash with ferruginous quartz, charcoal, powder, and copper. When the product was digested in nitric acid, glistening, needle-like crystals of this phosphide remained. The crystals were insoluble in hot or cold, conc. nitric acid, and dil. sulphuric acid. They were readily soluble in aqua regia. The crystals cannot be regarded as a solid soln. of iron tritaphosphide and hemiphosphide since the former is readily soluble in nitric acid. M. Boblique also reported the dipentitaphosphide, but H. le Chatelier and S. Wologdine could find no evidence of its existence. A. Granger obtained **iron tritetritaphosphide,** Fe_4P_3, to be formed by passing a current of phosphorus trichloride over reduced iron; the vapour of phosphorus diiodide acts similarly, but at a lower temp. H. Struve reported it to be formed in an impure state, but C. Freese doubted its existence. A. Granger's product lost its phosphorus at a red-heat. The grey, prismatic crystals were but little affected by aqua regia, but were freely attacked by chlorine, and fused alkali hydroxides. The analyses of the phosphides prepared by J. J. Berzelius, F. Wöhler, C. Hatchett, H. Davy, H. Struve, P. Berthier, and B. Pelletier corresponded with **iron hemiphosphide,** Fe_2P. It was obtained by C. Freese by heating a mixture of iron phosphate and lamp-black in a covered crucible for 4 hrs. at a white-heat. It appeared as a pale grey crystalline powder of sp. gr. 5·74. G. Maronneau obtained it by heating copper phosphide with one-tenth of its weight of iron turnings in an electric furnace, and isolating the product by treatment with conc. nitric acid. The sp. gr. was 6·57. H. le Chatelier and S. Wologdine made it in a similar manner, and from its elements, and by reducing iron phosphate by the aluminothermite process. This phosphide appears in pale grey, needle-like crystals. The conditions of stability are indicated in Figs. 25 and 26. C. Freese gave 5·74 for the sp. gr.; G. Maronneau, 6·57; and H. le Chatelier and S. Wologdine, 6·56. B. Sakalatwalla gave 1275° for the m.p.; N. S. Konstantinoff, 1350°; J. L. Haughton, 1380°; and H. le Chatelier and S. Wologdine, 1290°. The last-named gave 80° for the magnetic transformation point, and found it to be 50 times less magnetic than the tritaphosphide. The steel-grey prismatic crystals were found by J. J. Berzelius, H. Struve, and C. Freese to pass into ferric phosphate when heated in air; they were insoluble in all acids, and in a mixture of nitric and hydrofluoric acids. G. Tammann and H. Bredemeier studied the surface oxidation of the hemiphosphide, as well as the films produced by the halogens. H. Moissan said that this phosphide is attacked by fluorine at a red-heat. R. Schenck added ferrous sulphate to a flask from which phosphuretted hydrogen was being evolved by the action of potash-lye on phosphorus. The black pulverulent, and magnetic **iron ditritaphosphide,** Fe_3P_2, so obtained was washed by decantation, then with water, with alcohol, and with ether. It readily oxidized on exposure to air; and ignited below 100°, forming a reddish-brown powder. It dissolved slowly in dil. or conc. boiling acids, forming hydrogen and phosphine. C. Freese, A. Schrötter, and H. H. Hvoslef prepared **iron monophosphide,** FeP, by heating ferrous sulphide in a current of phosphine: $2FeS+2PH_3=2FeP+2H_2S+H_2$, or by passing a mixture of hydrogen and phosphorus vapour over red-hot iron; while H. le Chatelier and S. Wologdine made it by passing the vapour of phosphorus over red-hot, powdered iron hemiphosphide. L. M. Dennis and B. S. Cushman made it by heating ferric chloride at a red-heat with phosphine: $FeCl_3+PH_3=FeP+3HCl$. The black crystalline mass was found by A. Schrötter to have a sp. gr. of 5·21; and H. le Chatelier and S. Wologdine gave 5·76, and 48° for the magnetic transformation point. It was found to be 1·5 times more magnetic than the hemiphosphide. H. Rose reported **iron tetratritaphosphide,** Fe_3P_4, to be formed by the action of phosphine on gently warmed iron pyrites: $3FeS_2+4PH_3=Fe_3P_4+6H_2S$. C. Freese also obtained it by passing phosphine over heated iron, or ferrous chloride; and A. Granger by the action of phosphorus trichloride on red-hot iron. The dark grey powder has a sp. gr. 5·04. It passes into one of the lower phosphides when heated in hydrogen. According to H. Rose, the product gave the phosphorus flame when heated in the blowpipe flame; it dissolved in nitric acid and aqua-regia, but not in conc. or dil. hydrochloric acid. H. le Chatelier and S. Wologdine prepared **iron hemitriphosphide,** Fe_2P_3, by passing the vapour of phosphorus dichloride in a stream of hydrogen over reduced iron. A. Granger obtained this phosphide—*iron sesquiphosphide*—by carrying phosphorus vapour over heated ferric chloride by means of a current of carbon dioxide. H. le Chatelier and S. Wologdine found that the steel-grey crystals have a sp. gr. of 4·5. The magnetic permeability is one-seventy-fifth part of that of the monophosphide, and 30 times that of water. The permeability increases slowly as the temp. falls to —50°, but no magnetic transformation point could be found. According to A. Granger, the sesquiphosphide is insoluble in hydrochloric and nitric acids and in aqua regia; does not alter when heated in air to dull redness, but loses phosphorus at a bright red-heat; and is slowly attacked by chlorine at dull redness, and by bromine at a higher temp.

J. E. Stead showed that on melting sat. solid soln. of iron phosphide in iron and carbon alloys, the carbon causes a separation of phosphide near to the point of solidification, which appears as a eutectic in irregular-shaped areas; a residuum appears to be retained by the pearlite. E. D. Campbell and S. C. Babcock investigated the solubility of phosphorus in carbon steels. The ternary system: Fe–C–P, was studied by J. E. Stead, F. Wüst, and P. Goerens and co-workers. According to F. Wüst, the temp. at which sat. iron-carbon alloys begin to solidify is lowered by the addition of phosphorus, 1 per cent. of phosphorus causing a depression of 27°. When the proportion of phosphorus exceeds 6·7 per cent., the f.p. again rises. The ternary eutectic melts at 950°, and contains 6·7 per cent. P, 2·0 per cent. C, and 91·3 per cent. Fe. The eutectic disappears at a phosphorus content of 15 per cent., corresponding with the phosphide Fe_3P. Alloys containing between 6·7 per cent. and 15 per cent. of phosphorus show crystals of the phosphide.

The solubility of carbon in iron is reduced by the addition of phosphorus, but the temperature of formation of the eutectoid pearlite is not influenced by the presence of the phosphide. P. Goerens and W. Dobbelstein gave for the composition of the ternary eutectic *E*, Fig. 27, at 953°, 1·96 per cent. of carbon, 6·89 per cent. of phosphorus, and 91·15 per cent. of iron; and J. E. Stead, respectively 1·92, 6·89, and 91·19. In Fig. 26, *A* represents the iron-phosphorus eutectic, and *B*, the iron-carbon eutectic. They showed that when sat. solid soln. of iron phosphide in iron are heated or cooled they show no critical point at Ar_3, and the structure is not broken up even when the temp. exceeds 1000°. There can therefore be no allotropic change from β- to γ-iron by heating to 1000°. "When, however, carbon passes into the mass, a large proportion of the phosphide is expelled, and the carbon absorbed converts, at the temperature of the cementation furnace, a dominating proportion of the β-iron into γ-iron, and coincidentally the structure is entirely reorganized and recrystallization is effected. The recrystallization can only proceed coincidentally with the penetration of the carbon from the exterior towards the centre. Under favourable conditions the slowly developing crystalline grains develop longitudinally into columns, which radiate to the middle of the bar. A similar condition of crystalline development follows the change of allotropic state, but in the reverse direction, when carburetted steel is decarburized in ore or limestone at about 750°. At that temp. in presence of diffused carbide the carbon is in the γ-state, but as the carbon is removed β-iron is formed and crystallization of the iron proceeds from the exterior to the centre of the mass, leaving a most perfect columnar structure." J. O. Arnold and A. McWilliam showed that iron phosphide will diffuse from iron with 1·36 per cent. of phosphorus into pure iron when placed in close contact, and heated in vacuo for 10 hrs. at 1000°. The relative speeds of diffusion of carbon and phosphorus are as 5 : 1. J. E. Stead also noted this phenomenon. F. Osmond, H. M. Howe, and J. E. Stead observed that the Ac$_3$-critical temp. of iron is raised by phosphorus—0·417 changing the Ac$_3$ temp. from 820° to 870° if the initial ingot structure was removed by annealing, and to 950° if it was not removed. As F. Osmond puts it, phosphorus preserves the α-iron at a high temp. A. Carnot and E. Goutal found that hardening steel in the presence of manganese exerted no influence on the way iron and phosphorus combine. M. Lencauchez observed that when carbon dioxide acts on heated phosphorized pig-iron, carbon monoxide is formed by the abstraction of carbon from the iron, and much of the phosphorus is at the same time eliminated. According to J. E. Stead, the proportion of phosphine given off on dissolving phosphoretic irons free from carbon is approximately inversely in proportion to the amount of phosphorus. When 1·7 per cent. is present, only about 4 per cent. of it escapes as gas, whereas when there is only from 0·03 to 0·10 per cent., nearly 70 per cent. of it passes off as phosphine. When carbon is introduced into irons containing from 0·03 to 0·10 per cent. phosphorus, the proportion of phosphine liberated on solution of the metal steadily decreases with each increment of carbon, until, when the latter reaches about 1·2 per cent., only 15 per cent. of the whole escapes as phosphine. This behaviour leads to the conclusion that there are two soln. in steel above its solidifying point, a soln. of carbide and a soln. of phosphide; that the carbon soln. is the dominant one; and that the soln. of phosphide is conc. more and more into that portion of the iron not dominated by the carbon. The more the soln. of phosphide becomes conc. by the carbon, the less proportion of it is capable of yielding phosphine when it is treated with acid.

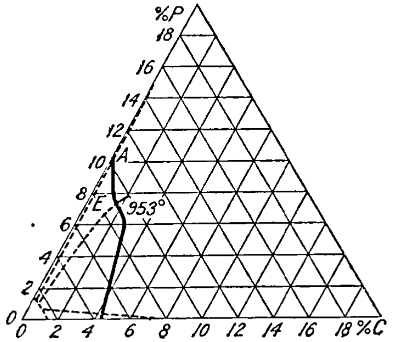

FIG. 27.—The Fusion Curves of a Portion of the Ternary System: Fe–C–P.

According to B. Pelletier,[28] an alloy of cobalt and phosphorus is formed when pieces of phosphorus are projected on red-hot cobalt; and by igniting a mixture of cobalt with glacial phosphoric acid and charcoal powder; while P. Berthier made the alloy by heating white-hot a mixture of cobalt or cobalt oxide, bone-ash, powdered quartz, and charcoal, and H. Rose, by the action of phosphine on heated cobalt chloride, or by igniting the phosphate in a stream of hydrogen. P. Kulisch found that phosphine precipitates a mixture of cobalt and its phosphide from ammoniacal soln., but it gives no precipitate with acid or neutral soln. I. Schepeleff and F. S. Schemtschuschny determined the f.p. curve for a number of alloys of cobalt and phosphorus, and the results are illustrated by Fig. 28. The tritaphosphide of cobalt corresponding with that of iron and of nickel does not appear on the diagram; but **cobalt hemiphosphide,** Co_2P, is formed. A. Granger made it by heating reduced cobalt at as high a temp. as possible in a porcelain tube through which the vapour of phosphorus trichloride is passed; and G. Maronneau obtained it by heating a mixture of copper phosphide and cobalt filings in an electric arc furnace for five minutes. The steel-grey mass consisting of needle-like crystals has a sp. gr. 6·4 at 15°. I. Schepeleff and F. S. Schemtschuschny gave 1386° for the m.p.; 4 for the hardness; and 6·3 to 6·6 for the sp. gr. It is less magnetic than the metal. According to A. Granger, and G. Maronneau, the phosphide is slowly decomposed by hydrochloric acid; is freely dissolved by nitric acid and by aqua regia; and it is decomposed by chlorine, and fused alkali hydroxides. H. Rose made **cobalt ditritaphosphide,** Co_3P_2, by passing phosphine over red-hot cobalt chloride; and by heating the phosphate in a current of hydrogen; while A. Schrötter made it by passing the vapour of phosphorus over reduced cobalt. The pale grey crystalline mass had a sp. gr. 5·62. H. Rose said that the black powder does not give the phosphorus flame when heated before the blowpipe; but when heated in chlorine it burns, forming phosphorus and cobalt chlorides. It is insoluble in conc. hydrochloric acid, but readily dissolved by nitric acid. By warming cobalt chloride at a dull red-heat, in phosphorus vapour, and boiling the products of the reaction with dil. hydrochloric acid, A. Granger obtained a black, non-magnetic brittle mass of **cobalt hemitriphosphide,** Co_2P_3. It decomposes at a bright red-heat; it is insoluble in hydrochloric and nitric acids, and in aqua regia; and is likewise attacked by chlorine at a high temp.

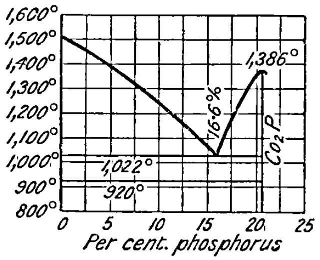

FIG. 28.—The Freezing-point Curves of Cobalt-Phosphorus Alloys.

According to B. Pelletier, a nickel phosphide is formed energetically when pieces of phosphorus are projected on red-hot nickel or by fusing a mixture of glacial phosphoric acid, nickel, and charcoal. W. A. Lampadius used similar processes. P. Berthier obtained a phosphide by fusing a mixture of nickel or nickel oxide, bone-ash, powdered quartz, and charcoal in a graphite crucible; H. Davy, by passing the vapour of phosphorus over red-hot nickel; C. F. Rammelsberg, by calcining the hypophosphite; and A. Oppenheim, by boiling a soln. of nickel oxide in aq. ammonia with phosphorus. P. Kulisch found that neutral and acid soln. of nickel salts are not changed by phosphine, but ammoniacal soln. give a black precipitate which is a variable mixture of nickel and its phosphide. N. S. Konstantinoff plotted the f.p. curve of alloys of nickel and phosphorus, and the results are shown in Fig. 29. Three nickel phosphides are indicated on the diagram. The first, **nickel tritaphosphide,** Ni_3P, freezes at about 965°, and it appears in rhombic plates; the second compound is **nickel dipentitaphosphide,** Ni_5P_2. Its formation was reported by B. Pelletier, W. A. Lampadius, and P. Berthier by the methods indicated above. A. Granger obtained it by the action of phosphorus trichloride on nickel at a red-heat; the product with phosphorus triiodide was not of constant composition. The dipentitaphosphide appears in needle-like or tabular crystals, which J. Garnier consider to be tetragonal. B. Pelletier said that the compound is non-magnetic and more fusible than nickel. The m.p. given by N. S. Konstantinoff is 1185°, and he found that there are two modifications with a transition point at 1035°. The β-dipentitaphosphide dissolves in the hemiphosphide, and the solid soln. separates into the hemiphosphide and α-dipentitaphosphide at about 1000°. A. Granger said that this phosphide loses phosphorus at a high temp., and is attacked by chlorine, and by molten alkali hydroxides. The third phosphide appearing on the f.p. diagram, Fig. 29, is **nickel hemiphosphide,** Ni_2P. H. Struve made it by heating nickel pyrophosphate alone at a white-heat, or in a stream of hydrogen; R. Schenck, by the method he employed for the iron phosphide (*q.v.*); A. Granger and co-workers, by heating reduced nickel in a current of phosphorus trichloride at about 600°; and G. Maronneau, by heating a mixture of copper phosphide and nickel filings for 5 minutes in the electric arc furnace. The products obtained by R. Schenck's process is black; the others give a greyish-white mass. The conditions of equilibrium are indicated in Fig. 29; and N. S. Konstantinoff added that it has a great tendency to crystallization, forming long, steel-grey needles. G. Maronneau gave 6·3 for the sp. gr. at 15°; and N. S. Konstantinoff, 1112° for the m.p. The hemiphosphide was found by A. Granger to lose some phosphorus when heated to a high temp. It is decomposed by chlorine, and fused alkali hydroxide; it is insoluble in acids; but freely soluble in a mixture of nitric and hydrofluoric acids. The product obtained by H. Davy, and A. Schrötter by the action of phosphorus vapour on nickel corresponded with **nickel ditritaphosphide,** Ni_3P_2; H. Rose obtained it by the action of phosphine on red-hot nickel sulphide or chloride, and he said that it is produced by calcining nickel pyrophosphate—but H. Struve obtained the hemiphosphide by this process. A. Schrötter gave 5·99 for the sp. gr. of the greyish-white mass. It is not affected by hydrochloric acid, but is easily dissolved by nitric acid. A. Granger reported **nickel hemitriphosphide,** Ni_2P_3, to be formed by passing phosphorus vapour in a stream of carbon dioxide over red-hot nickel chloride. The grey crystalline mass looks like graphite. It is not altered when heated to redness, but in the gas flame it loses phosphorus, and fuses to a metallic-looking mass. The hemitriphosphide is not magnetic; it is not affected by hydrochloric or nitric acid, or by aqua regia; chlorine attacks it when heated.

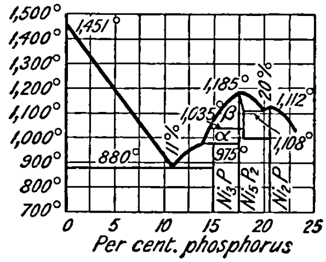

FIG. 29.—The Freezing-point Curves of Nickel-Phosphorus Alloys.

The association of phosphorus with iron and nickel in meteorites was recognized by J. J. Berzelius,[29] about 1832; and, on account of the slow solubility of the iron nickel phosphide in acids, C. U. Shepard called it a complex phosphide, *dyslytite*—from δύσλυτος, difficult to dissolve—and shortly afterwards, W. Haidinger called it **schreibersite**—after C. F. A. von Schreiber. The term schreibersite had previously been applied by C. U. Shepard to a chromium sulphide. Analyses of the **iron nickel phosphide** from various meteorites were made by N. W. Fischer, C. F. Rammelsberg, J. J. Berzelius, J. L. Smith, C. Bergemann, and H. Müller; and J. L. Smith summarized the results of his analyses by $Fe_2(Ni,Co)P$; S. Meunier gave a similar formula; and E. Cohen, $(Fe,Co,Ni)_3P$. C. von Reichenbach, and W. Haidinger disagreed on the use of the term schreibersite, and the former proposed the name *bamprite* or *iron glance* for a constituent of meteorites which had a metallic lustre and tin-white colour. This was shown to be mainly cohenite. F. Wöhler applied the term *partschite*—after P. M. Partsch—to a form of iron nickel phosphide occurring in meteorites in four-sided prismatic crystals; and G. Rose employed the term **rhabdite**—from ῥάβδος, a rod—for the complex phosphide occurring in minute tetragonal prisms or needles distributed parallel to the cubic edges of various meteoric irons. The term schreibersite then came to be applied to that constituent of these meteorites which occurred in steel-grey folia and grains; and rhabdite, to that occurring in needle-like crystals. Analyses were also made by C. Winkler, E. Cohen, A. Brezina and E. Cohen, E. Cohen and E. Weinschenk, E. D. Kislakowsky, N. S. Maskelyne, W. Flight, J. Domeyko, S. Meunier, C. A. Joy, H. Wichelhaus, A. Daubrée, B. Silliman and T. S. Hunt, E. Mallard, O. A. Derby,

E. Hussak, G. Florence, J. A. Antipoff, G. P. Merrill, W. Tassin, etc. H. E. Törnebohm reported schreibersite in the terrestrial iron of Ovifak, although E. Cohen could not find it there; G. vom Rath reported rhabdite in some pig-iron. A. Faye, E. Jannettaz, J. Garnier, and A. Daubrée discussed the synthesis of these phosphides. E. Mallard identified the iron phosphide he obtained as the result of a coal-mine fire —*vide supra*—with rhabdite. G. Tschermak, J. L. Smith, E. Cohen, and E. Cohen and E. Weinschenk showed that dyslytite, schreibersite, and rhabdite are probably the same thing; indeed, G. Tschermak found transition forms between acicular and foliated crystals—*i.e.* between schreibersite and rhabdite—in the meteorite of Braunau.

No definite *rhodium phosphide* has been reported. C. Claus[30] found that when the basic phosphate is heated in a current of hydrogen, the metallic-looking residue is a mixture of phosphorus and the metal. According to J. J. Berzelius, palladium unites with phosphorus at a high temp., forming a fusible *palladium phosphide.* R. Böttger found that when phosphine is passed into palladous salts, the precipitate is a mixture of phosphorus and metal. F. W. Clarke and O. T. Joslin obtained **iridium hemiphosphide,** Ir_2P, by projecting phosphorus on iridium at a white-heat. The product is as hard and resistant as iridium, and it loses its phosphorus when heated white-hot for some time. In this way, J. Holland was able to prepare objects of iridium shaped with the fusible alloy and afterwards converted into the iridium alone.

Platinum readily alloys with phosphorus. B. Pelletier[31] obtained an impure phosphide fusing platinum with glacial phosphoric acid and charcoal powder, and also by projecting phosphorus on red-hot platinum; E. Davy, by melting spongy platinum with phosphorus in an evacuated glass tube; and by heating ammonium chloroplatinate and phosphorus to dull redness; E. Davy, by the electrolysis of phosphoric acid with a platinum cathode; and W. C. Heraeus, by igniting magnesium pyrophosphate in a platinum crucible. According to A. Granger, phosphorus vapour acting on finely-divided platinum at 500° furnishes platinum diphosphide; at 600°, the pentatritaphosphide, and at a higher temp., the hemiphosphide. J. J. Berzelius also found that phosphorus vapour reacts with other platinum metals, forming, say, *palladium phosphide*, *iridium phosphide*, and *osmium phosphide.*

F. W. Clarke and O. T. Joslin prepared **platinum hemiphosphide,** Pt_2P, by heating the pentatritaphosphide; and A. Granger, by the action of phosphorus vapour on finely-divided platinum at 700°. The grey powder is sparingly soluble in aqua regia, and it is readily attacked by molten sodium carbonate. F. W. Clarke and O. T. Joslin prepared **platinum monophosphide,** PtP, along with the diphosphide by heating the pentatritaphosphide with aqua regia. A. Granger made **platinum pentitatriphosphide,** Pt_5P_3, by heating platinum sponge in phosphorus vapour at 600°; and F. W. Clarke and O. T. Joslin, by heating a mixture of platinum and phosphorus at a white-heat in a fireclay crucible. The silvery-white mass loses phosphorus when heated; and with aqua regia it furnishes the mono- and diphosphides. A. Schrötter, and A. Granger reported **platinum diphosphide,** PtP_2, to be formed by the action of phosphorus vapour on platinum at about 500°; and F. W. Clarke and O. T. Joslin, by heating the pentatritaphosphide with aqua regia. A. Schrötter gave 8·77 for the sp. gr. of the grey mass, and he found that when heated, it decomposes into the pentatritaphosphide and phosphorus. I. I. Saslawsky studied the mol. vol. It is insoluble in hydrochloric acid, and other acids, but soluble in aqua regia. It is decomposed by molten alkali hydroxides. P. Kulisch studied the action of phosphine on soln. of platinum chloride. The citron-yellow precipitate darkens, finally becoming nearly black. The proportion of platinum and phosphorus approaches that of the diphosphide—possibly **platinum dihydrodiphosphide,** PtH_2P_2. A. Cavazzi represented the reaction with phosphine: $PtCl_4+2PH_3=PtCl_2+2HCl+P_2H_4$; and $P_2H_4+PtCl_2=2HCl+PtH_2P_2$. The ochre-yellow product inflames in air between 100° and 110°; and also in contact with fuming nitric acid. It is insoluble in water and in hydrochloric acid.

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§ 13. The Lower Oxides of Phosphorus

The main oxides of phosphorus with their acids are:

	Acids.
(Phosphorus tetritoxide, P_4O)	——
(Phosphorus hemioxide, P_2O)	Hypophosphorus acid, H_3PO_2
Phosphorous oxide, P_4O_6	Phosphorous acid, H_3PO_3
— —	Pyrophosphorous acid, $H_4P_2O_5$
— —	Metaphosphorous acid, $(HPO_2)_n$
Phosphorus tetroxide, P_2O_4	Mixed acids, H_3PO_3 and H_3PO_4
— —	Hypophosphoric acid, $H_4P_2O_6$
Phosphoric oxide, P_2O_5	Phosphoric acid, H_3PO_4
— —	Pyrophosphoric acid, $H_4P_2O_7$
— —	Metaphosphoric acid, $(HPO_3)_n$
— —	Monoperphosphoric acid, H_3PO_5
— —	Diperphosphoric acid, $H_4P_2O_8$

There are derivatives of phosphorous and phosphoric acids like pyrophosphoric and metaphosphoric acids, etc.; and also some more or less doubtful oxides like phosphorus tetritoxide. The early investigators speak of the formation of a suboxide under various conditions, but the subsequent discovery of red phosphorus by A. Schrötter[1] proved that in many cases the alleged oxide was an allotropic form of phosphorus. This is considered to have been the case with the red substance formed by the incomplete combustion of phosphorus by oxygen under water—H. A. von Vogel, J. Pelouze, and R. Böttger; by the incomplete combustion of a thin layer of phosphorus spread over a porcelain capsule to keep down the temp. and washing the product with water to remove phosphoric acid, and with phosphorus trichloride to remove yellow phosphorus—U. J. J. Leverrier; by the incomplete oxidation of phosphorus by heating it with ammonium nitrate—R. F. Marchand; and by boiling the phosphorus with an aq. soln. of iodic or periodic acid—M. Bengieser.

U. J. J. Leverrier exposed to air a soln. of phosphorus in ether or in phosphorus trichloride, washed the product in warm water, and dried it in vacuo over sulphuric acid. The analysis corresponded with **phosphorus tetritoxide**, P_4O. B. Reinitzer and H. Goldschmidt obtained a similar product by the action of phosphorus oxychloride on zinc, magnesium, or aluminium at 100°, or on yellow phosphorus at 250°. They added that the substance obtained with yellow phosphorus has the composition of phosphorus tetritoxide, but not its properties. Its properties approximate closely to those of red phosphorus.

According to H. Biltz, ammonia acts energetically on phosphorus pentoxide at ordinary temp., forming a dark reddish-brown mass of phosphamic acid, which, when treated with water, forms phosphine, yellow phosphorus, and a reddish flocculent mass of phosphorus tetritoxide—not red phosphorus as H. Schiff supposed. A 0·06 per cent. yield of the same oxide was formed by heating phosphorus pentoxide at 250° either in vacuo or in a current of air, carbon dioxide, hydrogen, oxygen, or steam. Traces were also produced by dissolving the pentoxide in water or soda-lye.

The formation of the tetritoxide is said to be conditioned by the high temp., and by the presence of trioxide in the pentoxide. It is not formed by the action of a large excess of water, or ammonia; nor when the pentoxide has been purified by sublimation over platinum black in the presence of oxygen. Some tetritoxide was formed by heating the pentoxide for several hours at 230°, so that this treatment was not sufficient to remove all the trioxide which boils at 173°, or else the commercial pentoxide contains small quantities of other lower oxides of phosphorus. A. Stock observed the formation of the tetritoxide when yellow phosphorus is heated above its m.p. in liquid ammonia; the resulting black powder is considered to be a mixture of phosphamide and tetritoxide. The amide decomposes in presence of water, moist air, or acids; $2P_2NH_2+H_2O=P_4O+2NH_3$. Phosphorus tetritoxide is obtained by withdrawing water from hypophosphorous acid; thus, A. Michaelis and M. Pitsch made it by treating hypophosphorous acid with water: $4H_3PO_2=2P_2O+6H_2O$; $2P_2O=P_4O+O$; hydrochloric acid, acetyl chloride, or phosphorus trichloride can be used in place of water: $4H_3PO_2+2PCl_3=H_3PO_3+H_3PO_4+6HCl+P_4O$; but A. Geuther found that the actions of phosphorus trichloride on the acids of phosphorus furnish red phosphorus. C. H. Bothamley and G. R. Thompson said some tetritoxide is produced by the action of phosphorus trichloride on phosphoric acid—*vide infra,* the preparation of phosphorous oxide. Commercial hypophosphorous acid nearly always contains lime so that the product is affected accordingly.

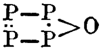
A. Michaelis and K. von Arend prepared the tetritoxide by evaporating hypophosphorous acid on a water-bath, mixing it with absolute alcohol and dry ether to remove the calcium salts. The alcohol and ether are distilled from the filtrate, and the residue evaporated on the water-bath. Thirty grms. of hypophosphorous acid so purified are dissolved in 100 grms. of glacial acetic acid, and treated with 90 grms. of acetic anhydride. The mixture was thoroughly mixed by shaking and poured into 1 to 2 litres of ice-cold water. The tetritoxide was allowed to settle; and, after decantation of the mother-liquor, washed with ice-cold water, and alcohol. The product was dried over phosphorus pentoxide in vacuo.

A. Michaelis and K. von Arend used ammonium hypophosphite in place of the acid: $5(NH_4)H_2PO_2=P_4O+H_3PO_3+6H_2O+5NH_3$. T. E. Thorpe and A. E. H. Tutton said that the tetritoxide is produced when phosphorus trioxide is decomposed by hot water. According to A. Michaelis and M. Pitsch, phosphorus dissolves in a mixture of one vol. of a 10 per cent. soln. of sodium hydroxide, and 2 vols. of alcohol, producing a dark red liquid with the elimination of hydrogen. When the filtered soln. is slowly acidified with dil. hydrochloric acid, a greenish-yellow precipitate of phosphorus tetritoxide is formed. The precipitate can be washed by decantation several times with hot water; collected on a filter, and washed successively with hot water, boiling alcohol, and ether. The product was dried on a porous plate in vacuo; and, after being ground to powder, again dried over phosphorus pentoxide for several days. This mode of preparation was also employed by A. Michaelis and K. von Arend, and D. L. Chapman and co-workers. A. Michaelis and M. Pitsch also obtained the tetritoxide by using solid hydrogen phosphide in place of phosphorus: $P_4H_2+H_2O=P_4O+2H_2$. A. Terni and C. Padovani obtained it by heating stannic chlorohypophosphite to 190°, and cooling the mass as soon as redding begins. On extraction with conc. hydrochloric acid, the tetritoxide remains undissolved.

The products obtained by these different processes vary in colour from dark brown through orange to scarlet-red, or even pale yellow, according to the state of subdivision. A. Michaelis and M. Pitsch gave 1·9116–1·9123 for the sp. gr. at 26°; and B. Reinitzer and H. Goldschmidt gave 1·48. The properties of the tetritoxides prepared by the action of zinc and of phosphorus on phosphoryl chloride are so different that B. Reinitzer and H. Goldschmidt suggested that two different forms of the tetritoxide exist. One form reduces salts of silver, gold, and mercury; the other does not. From the description of the properties of the product derived from the use of phosphorus, impure red phosphorus not the tetritoxide was in question.

A. Michaelis and M. Pitsch thus describe the properties of the tetritoxide When thoroughly dried, it is almost odourless, but a trace of moisture imparts to it the odour of phosphine; in the former condition, also, it may be heated in air to a comparatively high temp. without becoming ignited, but when moist it burns readily after being heated at 90° during several hours. If dried and heated in an indifferent gas, phosphorus distils over, leaving phosphoric oxide. Chlorine converts the dried oxide into phosphorus oxychloride and phosphorus pentachloride, the damp substance being oxidized to phosphoric acid, which is also produced by the action of sodium hypochlorite and of warmed sulphuric acid, the latter becoming reduced to hydrogen sulphide. Conc. nitric acid ignites the substance, which is indifferent towards hydrochloric acid. Many metals are precipitated by it from soln. of their salts either in metallic form, or as phosphorus compounds. A soln. of sodium or potassium hydroxide in aq. alcohol dissolves phosphorus tetritoxide, forming a deep red soln. which transmits only light between the C and D lines of the spectrum; when warmed, or on standing at the ordinary temp., this soln. evolves hydrogen and phosphine, sodium hypophosphite remaining dissolved. The oxide is coloured brown by ammonia, but the latter is removed on exposure to air, and the substance regains its orange-red hue. The presence of both alkali-lye and alcohol appear to be necessary for the dissolution of the tetritoxide; possibly an alcoholate is formed $NaO—P_4—OC_2H_5$, which is decomposed by acids or carbon dioxide and the tetritoxide precipitated: $NaO.P_4.OC_2H_5=P_4O+C_2H_5ONa$.

The analyses of the tetritoxide by U. J. J. Leverrier, B. Reinitzer and H. Goldschmidt, and A. Michaelis and M. Pitsch are in agreement with the empirical formula P_4O, which can be represented graphically:



$$\begin{matrix}P-P\\ \ddot{P}-\dot{P}\end{matrix}\!>O$$

G. le Bas also found this formula to be in harmony with the mol. vols. of the contained elements. A. Schrötter's view that the red product is impure red phosphorus was accepted by D. L. Chapman and co-workers because the analyses range from 86·50 to 94·52 per cent. of phosphorus, showing that the composition is variable, and hydrogen is present in considerable quantity. It is hence concluded that the alleged suboxide is red phosphorus whose microscopic particles have adsorbed water and undergone surface oxidation. A. Stock said that the samples of the tetritoxide which have been prepared retain hydrogen and water so tenaciously that the analyses *sehr annahernd den für* P_4O *berechneten Gehalt besitzt*. R. Schenck said that the tetritoxide behaves towards alcoholic alkali-lye like red phosphorus towards piperidine, and suggested that it is possibly a solid hydrogen phosphide mixed with finely-divided red phosphorus. A. Besson also regarded the tetritoxide as a mixture of red phosphorus, solid hydrogen phosphide, and phosphorus hemioxide. K. C. Browning considered that the tetritoxide can exist under certain unspecified conditions. A. Stock and co-workers, and A. Gutbier had doubts about the veritable existence of the tetritoxide as a chemical individual.

In the preparation of phosphorus tetritoxide by exposing to air for 24 hrs. yellow phosphorus under a layer of phosphorus trichloride, a thick white crust is formed on the surface of the phosphorus; and above and below this a yellow layer of a complex with the composition $4P_4O.3P_2O_5$. The phosphorus trichloride is decanted off, the pieces of phosphorus to which the complex adheres are separated from one another and put into water. The complex dissolves in water, forming a yellow soln. which is poured off from the phosphorus. At 80°, the product decomposes into phosphoric acid, and yellow flakes of a hydrated phosphorus suboxide of unknown composition.

According to A. Gautier,[2] when phosphorus trichloride is heated with crystalline phosphorous acid to 170° in a sealed tube, it furnishes a reddish-brown mass, the colour of which is due to the deposition of red phosphorus, according to the following equation: $3PCl_3+7H_3PO_3=4P+3H_4P_2O_7+9HCl$. If, however, the temp. is not allowed to rise beyond 79°–80°, hydrochloric and pyrophosphoric acids are still formed, but a bright yellow substance gradually separates, which may be purified by distilling off the excess of phosphorous chloride, and washing the residue with ice-cold water. The yellow powder thus obtained, dried first *in vacuo*, then at 140° in a current of carbon dioxide, has the composition of **phosphorus tetritahydroxide**, P_4HO. If the reaction is allowed to take place at a temp. above 80°, the product is contaminated with amorphous phosphorus. R. Boulouch obtained the same substance by dissolving phosphorus tetritiodide in potassium hydroxide: $P_4I+KOH=KI+P_4OH$; or by dissolving the tetritiodide in a soln. of potassium hydroxide, or carbonate, and adding hydrochloric acid to the liquor. The compound P_4HO is yellow, amorphous, unchangeable in dry air, but undergoes oxidation in moist air. It is insoluble in all the solvents employed, water, alcohol, ether, benzene, chloroform, essence of turpentine, even at 150°, glycerol, acetic acid, phosphorous acid, and phosphorous or antimonious chloride. It is a very stable body, and may be heated to 250° in dry carbonic anhydride, without losing weight. Towards 265° it evolves phosphine, and sets free a little common phosphorus, but it is only at 350°–360° that the phosphorus volatilizes freely, leaving an oxidized residue which attacks the glass. The compound is not affected by dil. acids, but ordinary nitric acid attacks it so violently as to produce a bright light. Water at 170° decomposes it easily, with evolution of pure phosphine—$2P_4HO+11H_2O=5PH_3O_2+PH_3O_3+2PH_3$. Very dil. alkaline soln. act upon the body P_4HO, causing the disengagement of a mixture of phosphine and hydrogen, and furnishing soln. of phosphate and hypophosphite, together with an insoluble brown substance, which when exposed wet to the air, seems to reproduce the original compound. Ammonia unites directly with P_4HO, producing a compound from which ammonia is withdrawn by the action of heat or of hydrochloric acid. A. Michaelis and M. Pitsch regard this hydroxide as a mixture of phosphorus tetritoxide and phosphorous acid. A. Gautier also found that the yellow powder often produced in the decomposition of phosphorus diiodide by water is similar in some respects to the preceding. It appears to be invariably formed when the iodide is decomposed by a large quantity of water. Analyses lead to the formula P_5H_3O, and the formation of the body may be explained by the following equation: $12PI_2+24H_2O=P_5H_3O+3PH_3O_4+3PH_3O_3+PH_3O_2+24HI$. During the reaction there is disengaged a quantity of phosphine, resulting from the further action of water upon the yellow body: $P_5H_3O+6H_2O=PH_3O_3+2PH_3O_2+2PH_3$. The compound P_5H_3O forms an unstable compound with ammonia. A. Michaelis and M. Pitsch consider this compound to be a mixture of phosphorus tetritoxide with solid hydrogen phosphide. K. I. Lissenko supposed the yellow precipitate to be hydrogen diphosphide. A. Gautier also found that when P_5H_3O is heated gradually to 275° in a current of carbon dioxide, it evolves phosphine, and leaves a residue which undergoes no further decomposition till the temp. is raised to 350°, and to which analysis assigns the formula, $P_{13}H_3O_3$: $3P_5H_3O=2PH_3+P_{13}H_3O_3$. Here again a mixture is probably involved and not a true compound.

A. Besson[3] reported that he had made **phosphorus hemioxide**, P_2O, (i) by warming a mixture of phosphoryl chloride and phosphonium bromide in a sealed tube at 50°: $POCl_3+PH_4Br=3HCl+HBr+P_2O$; (ii) by heating a conc. soln. of phosphorous acid and an excess of phosphorus trichloride in a reflux condensor: $PCl_3+H_3PO_3=3HCl+P_2O_3$; and $2P_2O_3=P_2O+P_2O_5$; and (iii) by the action of a current of air on a soln. of phosphorus in carbon tetrachloride. A. Besson said that the products obtained by the different processes are the same. The yellowish-red hemioxide is stable at 100°, but it gives off oxygen when heated to 135° in vacuo. It is not affected by water at ordinary temp., but when a mixture of the two is heated in a sealed tube at 100°, phosphorous acid is formed: $P_2O+O_2+3H_2O=2H_3PO_3$. It becomes incandescent in chlorine at ordinary temp.; chlorine dissolved in carbon tetrachloride forms phosphorus tri- or penta-chloride; bromine, phosphoryl bromide; and iodine, phosphorus diiodide. The hemioxide is probably contaminated with a little phosphorus and solid hydrogen phosphide; and A. Michaelis and M. Pitsch hold that it is the tetritoxide contaminated with some acids of phosphorus as well. K. Weidner supported A. Michaelis and M. Pitsch's assumption that A. Stock and M. Rudolph said that this compound may possibly be formed by the action of acids on a soln. of P_4S_3 in alkali-lye. If these contain the hemioxide, there is no relation between it and H_3PO_2; though the anhydride of this acid, P_2O, is the hemioxide, just as the anhydride of phosphorous acid is P_2O_3, and of phosphoric acid, P_2O_5. L. J. Chalk and J. R. Partington were unable to prepare the hemioxide. The product obtained by following A. Besson's directions is somewhat variable in composition and appears to be a mixture of finely divided amorphous phosphorus with strongly adsorbed phosphorous acid, although, especially when prepared at lower temp., solid hydrogen phosphides may be present. The amount of oxygen present is always much less than is required by the formula P_2O, and hydrogen also is always present, even after prolonged drying over phosphorus pentoxide.

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§ 14. Hypophosphorous Acid

In 1816, P. L. Dulong[1] reported the isolation of the salt of *l'acide au minimum d'oxygène*, which he proposed to name *acide hypophosphoreux*, **hypophosphorous acid**, H_3PO_2. It was obtained from the liquid produced when the phosphides of alkaline earths are treated with water. In the following year, H. Rose investigated a whole series of salts of this acid.

P. L. Dulong showed that hypophosphorous acid or its salts are formed by the decomposition of phosphides of the alkaline earths by water ; and H. Rose, by boiling phosphorus with milk of lime, baryta-water, or an aq. or alcoholic soln. of potassium hydroxide. The following process has been recommended—*vide infra*, calcium hypophosphite :

Two kgrms. of quicklime are slaked with about 5 litres of water, and then added to 20 litres of water contained in an iron boiler. Then add about 0·5 kgrm. of phosphorus. Keep the mixture boiling and add more water from time to time to make up for that lost by evaporation. During this process there is a continued evolution of spontaneously inflamed phosphine. When the strong odour of phosphine ceases to be given off, the soln. is filtered and the residue is washed. The residue is composed of the excess of calcium hydroxide and phosphate—about half the phosphorus is converted into phosphate. The soln. and washings are then concentrated, and again filtered to remove a small quantity of calcium carbonate which has been formed by the action of the air on the lime in soln. The concentrated liquid is now evaporated until a pellicle forms, when the calcium hypophosphite crystallizes ; or the heat may be continued, the liquid being constantly stirred, until the salt is obtained in a granular form. A soln. of the calcium hypophosphite is then treated with 1·37 times its weight of oxalic acid ; and the clear filtrate evaporated as required.

J. A. Kendall found it advantageous to mix charcoal with the phosphorus before adding the latter to the milk of lime or other hydrate used. The charcoal or powdered coke is made into a thin cream with water and mixed by heat and agitation with the phosphorus. When cold, the mixture is added to the milk of lime in the usual way. C. A. Wurtz made the hypophosphite by boiling a soln. of barium sulphide with phosphorus; A. Winkler, by the action of phosphine on aq. soln. of the alkali or alkaline earth hydroxides; A. Cavazzi, by the action of phosphine on sulphurous acid in the presence of mercury at 60°–70°: $PH_3+H_2SO_3+Hg=H_3PO_2+H_2O+HgS$; C. A. Wurtz, by the slow oxidation of hydrogen hemiphosphide; A. Michaelis and co-workers, by heating phosphorus tetritoxide in moist air; W. Ipatieff and W. Nikolaieff, by the action of hydrogen, at 250 to 300 atm. press., and 360° to 400°, on lead phosphate; and A. Oppenheim, by heating phosphorus with syrupy phosphoric acid at 200°.

P. L. Dulong filtered the liquid obtained by the action of water on barium phosphide to remove the barium phosphate; added dil. sulphuric acid to precipitate barium sulphate, and evaporated the filtered soln. of hypophosphorous acid at 80° to 90° to a syrupy consistency. J. Thomsen cooled the conc. aq. soln. to 0°, and obtained crystals of the acid. A. Geuther, E. Merck, and C. Marie employed a similar process. G. Lunau obtained a soln. of the acid by treating the calcium salt with oxalic acid. H. Rose treated the barium salt with an excess of sulphuric acid, digested the filtrate with an excess of lead monoxide, and treated the filtered soln. of basic lead hypophosphite with hydrogen sulphide; and, after filtering off the lead sulphide, concentrated the soln. of phosphoric acid by evaporation. C. Marie treated the sodium salt with the calculated amount of sulphuric acid, extracted the hypophosphorous acid by shaking the liquid with absolute alcohol, and evaporated the alcoholic soln. in vacuo. The commercial acid usually contains calcium salts. A. Michaelis and K. von Arend purified the acid by evaporating it on a water-bath, then adding absolute alcohol and dry ether; filtering the liquid from sediment; distilling off the alcohol and ether; and evaporating the residue on a water-bath. G. Heikel purified the acid by adding ammonium oxalate to the aq. soln. The filtered soln. of ammonium hypophosphite was treated with barium carbonate and boiled until the smell of ammonia disappeared. The barium salt was then decomposed by the calculated quantity of sulphuric acid as indicated above.

The early workers described hypophosphorous acid as a colourless, viscid, non-crystallizable liquid; but J. Thomsen was able to induce the crystallization of the syrupy liquid by rubbing the walls of the glass containing vessel with a glass rod at 0°. C. Marie purified the acid by fractional crystallization, and started the crystallization by seeding the syrupy liquid with a crystal of the acid. C. A. Wurtz gave 1·493 for the sp. gr. of the syrup at 18·8°; and A. Geuther, 1·49 at 10°. A. Michaelis and K. von Arend gave 1·4625 for the sp. gr. of the crystals. M. Wien measured the relation between the viscosity and electrical conductivity of aq. soln. of the acid. J. Thomsen said that the crystals gradually melt at ordinary temp. in air, but the liquid solidifies again when surrounded by cold water; he gave 17·4° for the m.p.; while C. Marie gave 26·5° for the m.p. of the acid. The melted acid has a great tendency to undercooling. According to P. L. Dulong, the acid decomposes when heated giving off phosphorus vapour; but H. Rose showed that phosphine and phosphoric acid are the products of decomposition: $4H_3PO_2=2PH_3+2H_3PO_4$. C. Marie said that the thermal decomposition occurs in two phases: Above 100°—and rapidly between 130° and 140°—the reaction is symbolized: $3H_3PO_2=PH_3+2H_3PO_3$; and above 140°—and rapidly between 160° and 170°: $4H_3PO_3=PH_3+3H_3PO_4$. N. R. Dhar found that the decomposition of hypophosphorous acid into phosphine and phosphoric acid is retarded by mild reducing agents. E. Cornec measured the lowering of the f.p. of soln. of hypophosphorous acid when progressively neutralized by sodium hydroxide. The resulting simple V-curve is characteristic of monobasic acids. Similar results were obtained with aq. ammonia in place of the soda-lye. J. Thomsen gave for the heat of formation of the crystallized acid $(3H,P,O_2)=139·950$ to $139·970$

Cals.; 137·550 to 137·660 Cals. for the fused acid; and 139·750 to 139·800 Cals. for the aq. soln. J. Thomsen's value for the heat of fusion is 2·4 Cals.; and for the heat of soln., —0·2 to —0·17 Cal. for the crystals, and 2·2 to 2·14 Cals. for the fused acid. E. Petersen gave 0·713 Cal. for the heat of dilution. P. A. Favre and J. T. Silbermann gave 48·3 Cals. for the heat of oxidation. J. Thomsen found the heat of neutralization for $n\mathrm{H_3PO_2}$aq.+NaOHaq. to be 15·4, 15·2, and 7·6 Cals. for $n=2$, 1, and 0·5 respectively; and for $\mathrm{H_3PO_2}+\frac{1}{2}\mathrm{Ba(OH)_2}$, 15·46 Cals. This is taken to favour the assumption that the acid is monobasic. J. C. Thomlinson attempted to obtain evidence in the chemical constitution of this acid from the thermochemical data. P. A. Favre and J. T. Silbermann gave for the relative thermal eq. of hypophosphorous, phosphorous, and phosphoric acids, respectively, 1; 2·91; 4·36. O. Stelling studied the X-ray spectrum. W. Ostwald found the mol. electrical conductivity of aq. soln. with a mol of hypophosphorous acid in v litres, at 25°, to be

v .	2	4	8	16	32	64	128	256	512	1024
μ .	140	172	207	245	281	312	335	352	361	367
α .	0·360	0·442	0·532	0·630	0·722	0·802	0·861	0·905	0·925	0·9148
K .	0·1012	0·0876	0·0757	0·0670	0·0587	0·0508	0·0417	0·0336	0·0234	0·0154

The values for α, the degree of ionization, and the ionization constant, k, are derived from the mass-law equation $K=\alpha^2(1-\alpha)v$, on the assumption that S. Arrhenius' value, 389, represents the mol. conductivity at infinite dilution. A. D. Mitchell found K to be more nearly constant by writing $K=\alpha^2(1-\alpha)v=0{\cdot}1015-\frac{1}{35}\log v$. I. M. Kolthoff found that the ionization constant increases from $K=0{\cdot}01$ in a 0·001M-soln. to $K=0{\cdot}062$ in 0·05M-soln. at 18°; allowing for the activity of the ions, K increases from 0·020 for 0·001M-soln. to 0·053 for 0·1M-soln. Hypophosphorous acid behaves as a strong monobasic acid, and it can be titrated using methyl orange as indicator. A. D. Mitchell also measured the ionization of hypophosphorous acid in the presence of hydrochloric acid by the hydrolysis of methyl acetate process, and found the results to be in accord with the rate that in a mixture of two electrolytes, each is ionized to the same extent as it would be if present alone in a soln. having the same conc. of ions. W. Ostwald's values for the effect of temp. on the conductivity of N-$\mathrm{H_3PO_2}$ are indicated in Fig. 30. H. Wegelins examined the effect of conc. on the optimum temp. of the conductivity. S. Arrhenius represented the temp. coeff. of the mol. conductivity of soln. with n-gram-equivalent per litre, at 35° by 0·0148 for $n=0{\cdot}001$; 0·0110 for $n=0{\cdot}01$; 0·0058 for $n=0{\cdot}1$; and 0·0041 for $n=0{\cdot}5$. The effect of temp., θ, on the conductivity, λ, can be represented by $\lambda=\lambda_0e^{-0{\cdot}00992(1+0{\cdot}01455\theta)}$, which is a maximum when θ_0 corresponding with λ_0 is 25°. Hence the maximum occurs at 57°. E. Blanc measured the neutralization curve with the progressive addition of sodium hydroxide, and obtained for the ionization constant $K_1=0{\cdot}06$. S. Arrhenius also calculated the heat of ionization to be —3·63 Cals. G. Bredig gave for the transport number 41·8. P. Pascal made observations on the magnetic properties of the acid.

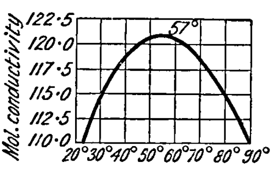
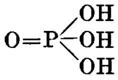


FIG. 30.—The Effect of Temperature on the Molecular Conductivity of Solutions of Hypophosphorous Acid.

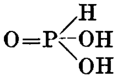
Analyses by P. L. Dulong, A. Geuther, and H. Rose are in agreement with the empirical formula $\mathrm{H_3PO_2}$. C. A. Wurtz, A. Geuther, and J. Thomsen showed that the salts of the acid indicate that hypophosphorous acid is monobasic, and two of the three hydrogen atoms are part of the acid radicle. P. Walden also found the electrical conductivity of the salt in harmony with the same hypothesis. A. L. Ponndorf assumed that the acid contains two hydroxyl groups and one hydrogen atom united to tervalent phosphorus, namely, $\mathrm{H.P(OH)_2}$. This agrees with P. Pascal's observations on the magnetic properties of the acid. Following

A. Lieben, however, it is generally assumed that the phosphorus is quinquevalent in phosphoric, phosphorous, and hypophosphorous acids:



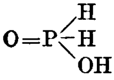
$$\mathrm{O{=}P}{<}\begin{matrix}\mathrm{OH}\\\mathrm{OH}\\\mathrm{OH}\end{matrix}$$

Phosphoric acid (Tribasic).



$$\mathrm{O{=}P}{<}\begin{matrix}\mathrm{H}\\\mathrm{OH}\\\mathrm{OH}\end{matrix}$$

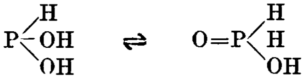
Phosphorous acid (Dibasic).



$$\mathrm{O{=}P}{<}\begin{matrix}\mathrm{H}\\\mathrm{H}\\\mathrm{OH}\end{matrix}$$

Hypophosphorous acid (Monobasic).

The last formula emphasizes the monobasicity of the hypophosphorous acid, and it agrees with O. Stelling's observations on the X-ray spectrum. It is probable that one of the hydrogen atoms is labile, corresponding with the desmotropic change:



$$\mathrm{P}{<}\begin{matrix}\mathrm{H}\\\mathrm{OH}\\\mathrm{OH}\end{matrix} \rightleftharpoons \mathrm{O{=}P}{<}\begin{matrix}\mathrm{H}\\\mathrm{H}\\\mathrm{OH}\end{matrix}$$

because, although dibasic inorganic hypophosphites are not known, yet the so-called *alkyl-phosphinic acids*, formed by oxidizing the secondary phosphines with fuming nitric acid, are to be regarded as derivatives of hypophosphorous acid. *Dimethyl phosphinic acid*, $(CH_3)_2PO.OH$, resembles paraffin, it melts at 76°, and volatilizes without decomposition. A corresponding *diethyl-dithio-phosphinic acid*, $(C_2H_5)_2PS.SH$, is known. The tendency of phosphorus to pass into the $O{=}P{\equiv}$ form is illustrated by the action of heat on this acid, and on its salts, for phosphoric acid and phosphine are produced: $2H_3PO_2{=}OP(OH)_3{+}PH_3$. According to A. Geuther, neither the anhydride, P_2O, nor the chloride, PCl, corresponding with hypophosphorous acid is known. L. Lendle, and G. Schick found that the barium salts of phosphorous acid or of hypophosphorous acid, prepared at high and low temp., reduce silver and mercury salts with very different velocities; and they assumed that there are two different forms of hypophosphite or phosphite. They associated the assumed alteration in the constitution of the hypophosphites with the change in the conductivity which occurs with variations of temp.—Fig. 30, for the active form is obtained at a low temp., the inactive form at a high temp. H. Gorke, however, showed that the active form is contaminated with acid. H. Burgarth, H. Remy, and T. M. Lowry's observations made observations on the electronic structure of hypophosphorous acid, *vide supra*, phosphoric acid.

While C. A. Wurtz[2] said that **hydrogen** in *statu nascendi* reduces hypophosphorous acid to phosphine, A. L. Ponndorf observed no reduction at all in acidic or alkaline soln. C. F. Rammelsberg found that when exposed to **air**, hypophosphorous acid oxidizes to phosphorous acid, and then to phosphoric acid. A. Benrath and K. Ruland observed that hypophosphorous acid is oxidized to phosphorous acid in the presence of ceric sulphate. E. Rupp and A. Finck said that the speed of oxidation of hypophosphorous acid is small in alkaline soln., but increases proportionally with the acidity of the soln. A. Michaelis and M. Pitsch obtained phosphorus tetritoxide (*q.v.*) by the action of **water** on this acid. N. Bakh said that when the reaction $NaH_2PO_2{+}H_2O{=}NaH_2PO_3{+}H_2$ is catalyzed by palladium-black, the quantities of various poisons required per mol of palladous chloride are: potassium cyanide, 1·75 mols; mercuric chloride, 1 mol; thiocarbamide, 1·5 mols; and quinine hydrochloride, over 10 mols. Alkaloids generally have a relatively weak action on catalysts. The poisoning effect is due partly to chemical combination between the palladous chloride and the poison, yielding a compound which cannot be reduced by sodium hypophosphite, and partly to adsorption on the surface of the palladium-black. With colloidal palladium, the effect is one of adsorption, and again a definite number of mols of the poison is required to saturate the surface of the palladium particles and paralyze their action. I. M. Kolthoff, and M. Major studied the oxidation of hypophosphites by **hydrogen dioxide.** P. L. Dulong showed that the acid is oxidized by **chlorine** in aq. soln. I. M. Kolthoff, and F. X. Moerk oxidized soln.

of the acid for analytical purposes by chlorine, and **bromine.** According to E. Rupp and A. Finck, the acid is slowly oxidized by **iodine**, forming phosphorous acid and not phosphoric acid in acidic soln.: $H_3PO_2+I_2+H_2O=H_3PO_3+2HI$; and to phosphoric acid in the presence of an excess of sodium hydrocarbonate: $H_3PO_2+2I_2+2H_2O=H_3PO_4+4HI$. An analytical process for the determination of hypophosphorous and phosphorous acids in a given mixture has been based on these facts. This was studied by I. M. Kolthoff. B. D. Steele found that the speed of oxidation of hypophosphorous acid by iodine in acid soln. is independent of the conc. of the iodine provided there is more than about $0{\cdot}004N$-I_2 present—the limiting value of this conc. varies with the initial conc. of the acid. The reaction is unimolecular with respect to hypophosphorous acid, but it is catalytically accelerated by $H^{\cdot}$-ions. Since $H^{\cdot}$-ions are produced during the course of the reaction, in the absence of any large initial conc. of the acid, the reaction undergoes autocatalytic acceleration. The velocity constant k is 0·043 at 18°, and 0·095 at 25°; it varies within narrow limits with the initial conc. of the hypophosphorous acid and the added acid: $\log k=0{\cdot}1134\theta-5{\cdot}1879$. The rise in the value of k is about 0·031 per 10°. A. D. Mitchell found that the effect of the conc. of the iodine is slight at moderate dilutions, but is relatively large at greater dilutions where the conc. of the I_3'-ion is; and the effect of the hydrochloric and hydriodic acids on the ionization of the hypophosphorous acid should be considered. It is assumed that the oxidation of hypophosphorous acid takes place in two stages. The known facts are explained by assuming that the non-ionized mols. of hypophosphorous acid are in equilibrium with a small proportion of active H_5PO_3-molecules: $H_3PO_2+H_2O\rightleftharpoons H_5PO_3$, which react rapidly with iodine: $H_5PO_3+I_3'\rightarrow H_3PO_3+2H^{\cdot}+3I'$; and the restoration of the equilibrium so displaced is accelerated by $H^{\cdot}$-ions, and forms the measurable reaction $H_3PO_2+H_2O\rightleftharpoons H_5PO_3$. The reaction was studied by M. Boyer and M. Bauzil, and A. Brukl and M. Behr. A. L. Ponndorf observed that no reaction occurs with **hydrochloric acid** at 100°; but A. Michaelis and M. Pitsch obtained phosphorus tetritoxide (*q.v.*), or impure red phosphorus, by the action of this acid—particularly with alcoholic soln. A. L. Ponndorf said that with **hydriodic acid** there is a vigorous reaction: $3H_3PO_2+HI=2H_3PO_3+PH_4I$. W. Ostwald found hypophosphorous acid accelerates the reaction between hydriodic and hypobromous acids. D. Vitali represented the reaction with **potassium iodate**: $KIO_3+H_3PO_2=KH_2PO_2+HIO_3$; and $HIO_3+3KH_2PO_2=3KH_2PO_3+HI$; as well as $5HI+HIO_3=3I_2+3H_2O$; and $3I_2+3KH_2PO_3+3H_2O=6HI+3KH_2PO_4$; the **chlorates** and **bromates** are not reduced. K. A. Hofmann found that in the presence of a trace of osmium tetroxide, a neutral or slightly acid soln. of potassium chlorate oxidizes hypophosphorous acid to phosphoric acid.

According to A. L. Ponndorf, and R. Rother, **sulphur dioxide** acts on hypophosphorous acid, forming sulphur and phosphorous acid; and L. Maquenne said that in aq. soln., there is a momentary formation of hyposulphurous acid before the sulphur separates. O. von Dienes said that sulphur dioxide—gaseous or in aq. soln.—can be reduced to hydrogen persulphide by hypophosphorous acid. C. A. Wurtz observed that when warmed in the presence of conc. **sulphuric acid**, phosphoric acid is produced with the separation of sulphur and the evolution of some sulphur dioxide. A. Gutbier and E. Rohn found that alkaline soln. of **selenious acid** are reduced to selenium, and in acidic soln., to hydrogen selenide; while soln. of **selenic acid** are scarcely affected by hypophosphorous acid. A. Gutbier found that tellurium is precipitated from soln. of **tellurous acid**, and of **telluric acid.** H. Rose found that **nitric acid** oxidizes hypophosphorous acid to phosphoric acid. A. Geuther said that soon after the acid has been added and the soln. is warm, red fumes are given off and the hypophosphorous acid is converted into phosphorous acid; and when the soln. is evaporated, more red fumes are evolved and the phosphorous acid is converted into phosphoric acid. A. Michaelis and M. Pitsch found that a conc. aq. soln. of hypophosphorous acid forms phosphorus tetritoxide (*q.v.*) when treated with **phosphorus trichloride**; and, according to

A. Geuther, the reaction is as follows: $3H_3PO_2+PCl_3=2P(OH)_3+2P+3HCl$. Orthophosphoric acid is also produced, but this probably arises from the action of phosphorus trichloride on phosphorous acid. These results agree with $H.P(OH)_2$ for the formula of hypophosphorous acid. The action of **phosphorus oxychloride** is similar to that of the trichloride, but the reaction is more energetic, and after it has ceased, a fresh reaction may be produced by heating the mixture to 100°. The two stages may be represented as follow: (i) $6H_3PO_2+3POCl_3=3HPO_3+2P(OH)_3+4P+9HCl$; (ii) $2P(OH)_3+3POCl_3=3HPO_3+2PCl_3+3HCl$. The former reaction is probably the resultant of the following: $6H_3PO_2=2PH_3+4P(OH)_3$; followed by $4P(OH)_3+3POCl_3=3HPO_3+2PCl_3+3HCl+2P(OH)_3$; and by $2PH_3+2PCl_3=4P+6HCl$. Hypophosphorous acid thus behaves like a mixture of phosphine and phosphorous acid; and when it is heated to 110°–115°, it is decomposed into these substances; but when the temp. reaches 250° the phosphorous acid itself decomposes. The action of **phosphorus pentachloride** on hypophosphorous acid is energetic, red phosphorus being deposited; but after sufficient of the pentachloride has been added, and the mixture has been heated, nothing remains but phosphorus oxychloride and phosphorus trichloride. The reactions are probably as follow: $3H_3PO_2+6PCl_5=6POCl_3+PCl_3+2P+9HCl$; followed by $6H_3PO_2+6POCl_3=6HPO_3+2PCl_3+4P+12HCl$; $6HPO_3+12PCl_5=18POCl_3+6HCl$; and $6P+9PCl_5=15PCl_3$; the resultant reaction being $H_3PO_2+3PCl_5=2POCl_3+2PCl_3+3HCl$. A. Michaelis and M. Pitsch said that **acetic anhydride** withdraws the elements of water from hypophosphorous to furnish phosphorus tetritoxide (*q.v.*), and **acetyl chloride** gives the same product: $9H_3PO_2+12CH_3COCl=H_3PO_4+2P_4O+12CH_3COOH+12HCl$, as well as: $5H_3PO_2+6CH_3COCl=H_3PO_3+P_4O+6CH_3COOH+6HCl$; and there is a side reaction, $4H_3PO_2=H_3PO_4+H_3PO_3+H_2O+P_2H_4$. J. Ville studied the action of hypophosphorous acid on various **aldehydes**; R. Fosse, on aromatic **alcohols**, aldehydes, and **ketones**; and C. Marie, on **acetone.** J. Mai found that hypophosphorous acid readily converts the **diazo-salts** into hydrocarbons. H. W. Jones found that the acid dissolves **strychnine** and **morphine.** Hypophosphorous acid attacks **glass** and **porcelain** more rapidly than phosphoric acid.

According to F. Loessner, when a soluble hypophosphite is heated with a conc. soln. of **alkali hydroxide,** the salt is oxidized: $NaH_2PO_2+NaOH=Na_2HPO_3+H_2$. The reaction is unimolecular, and the velocity is nearly doubled by a rise of temp. from 92°–100°. Eq. proportions of sodium and potassium hydroxides have the same influence. The velocity constant, *k*, increases with increasing conc. of alkali-lye, but not proportionally; thus with

	NaOH				KOH	
	1·23*N*-	2·43*N*-	3·94*N*-	4·90*N*-	2·4*N*-	4·42*N*-
k . .	0·00041	0·00152	0·00516	0·00983	0·00166	0·00787

According to P. L. Dulong, and H. Rose, hypophosphorous acid reacts with some metal oxides producing hypophosphites; others are reduced to metals; others to hydrides. Thus, H. Rose represented the reaction with **copper sulphate:** $Ba(H_2PO_2)_2+4CuSO_4+4H_2O=2H_3PO_4+BaSO_4+3H_2SO_4+4Cu$; on the other hand, C. A. Wurtz, C. F. Rammelsberg, and W. Muthmann and F. Mawrow said that with a soln. of cupric sulphate, copper hydride is formed; or else copper accompanied by the evolution of hydrogen if the temp. exceeds the decomposition temp. of the hydride. The reaction was studied by M. Major. S. Ramachandran showed that the reduction occurs only when the soln. is distinctly acid. According to A. Sieverts, if an excess of the hypophosphite be employed, the precipitate, when heated, gives off hydrogen and forms a red spongy mass of copper; on the other hand, if an excess of the copper salt be present, a brownish-yellow precipitate is formed, which, on boiling, furnishes a crystalline powder of copper. In all cases, cuprous salts are produced as an intermediate stage in the reduction. In the reaction between copper sulphate and hypophosphorous acid, the quantity of hydrogen set free does not depend upon the amount of cuprous hydride formed, but rather on the amount of hypophosphorous acid present. The evolution of gas is caused by the copper-sponge resulting from the decomposition of the hydride, and the action continues so long as any hypophosphorous acid remains undecomposed. E. J. Bartlett and W. H. Merrill consider that the action is due to the formation of a cupric hydride which acts catalytically on the hypophosphorous acid, oxidizing it to phosphorous acid and liberating hydrogen: $H_3PO_2+H_2O=H_3PO_3+H_2$, just as palladium hydride, according to R. Engel, oxidizes barium hypophosphite to the phosphite with the evolution of hydrogen by a continuous action without appreciably affecting the hydride. If a syrupy soln. of hypophosphorous acid be treated with cupric hydride, a mixture of phosphine and hydrogen is given off which is not spontaneously inflammable. A. Sieverts and F. Loessner consider that the metal and not the hydride is the catalyst, since palladium precipitated by carbon monoxide is virtually free from hydrogen, and yet it decomposes hypophosphites. The reaction is discussed in connection with copper hydride—**3**. 21, 6. J. B. Firth and J. E. Myers showed that with an acidic soln. of copper sulphate, sodium hypophosphite produces a substance which appears to be a mixture of cuprous oxide, hydride, and phosphate. A. D. Mitchell showed that with cupric chloride, the first stage of the reduction results in the change of hypophosphorous acid *molecules* to the active form, provisionally formulated as H_5PO_3; this change is catalyzed by hydrogen ions. In dil. copper soln. two succeeding reactions have been detected: (i) an equilibrium in which the copper ion and the active hypophosphorous acid give a complex ion ($X^{\cdot\cdot}$) and hydrogen ions, which therefore repress the reaction: $H_5PO_3+2Cu^{\cdot\cdot}=X^{\cdot\cdot}+2H^{\cdot}$; and (ii) a direct reaction between the complex and chloride ions: $X^{\cdot\cdot}+2Cl'=Cu_2Cl_2+H_3PO_3$.

P. L. Dulong observed that hypophosphorous acid reduces soln. of **silver salts**. The reaction was studied by M. Major, and C. F. Rammelsberg. A. Sieverts and co-workers said that the reaction with silver nitrate may be attended by the evolution of hydrogen: $2NaH_2PO_2+2AgNO_3+4H_2O=2H_3PO_4+2NaNO_3+2Ag+3H_2$; or hydrogen may not be evolved: $NaH_2PO_2+4AgNO_3+2H_2O=H_3PO_4+NaNO_3+3HNO_3+4Ag$. There are complications owing to the reduction of the anion. A soln. of silver phosphate is reduced to the metal by hypophosphorous acid; and even in ammoniacal soln., the precipitate is silver, not silver suboxide; and there is no evidence of the formation of silver hydride reported by E. J. Bartlett and W. F. Rice—*vide* **3**. 22, 7. A. D. Mitchell found that in the reduction of silver nitrate, the reaction, $2AgNO_3+H_3PO_2+H_2O=2Ag+2HNO_3+H_3PO_3$, is also attended by $4AgNO_3+H_3PO_2+2H_2O=4Ag+4HNO_3+H_3PO_4$. He found that hypophosphorous acid reduces silver nitrate at the same rate as, *ceteris paribus*, it reduces iodine, mercuric chloride, or cupric chloride. This rate is independent of the conc. of the substance undergoing reduction, provided it exceeds a definite value, which is $N/50$ in the case of silver nitrate, and is ascribed to a change involving the formation of an active form of the acid. P. L. Dulong observed that soln. of **gold salts** are reduced by hypophosphorous acid; and, added A. Sieverts, the precipitate slowly oxidizes a boiling soln. of the acid, and hydrogen is evolved. The reaction was also studied by M. Major. H. Rose found that soln. of **mercuric chloride** are reduced to mercurous chloride and to mercury. The reaction was studied by A. Sieverts. The oxidation of hypophosphorous to phosphorous acid proceeds relatively quickly, $H_3PO_2+2HgCl_2+H_2O=H_3PO_3+Hg_2Cl_2+2HCl$; and that of phosphorous to phosphoric acid relatively slowly, $H_3PO_2+4HgCl_2+2H_2O=H_3PO_4+2Hg_2Cl_2+4HCl$. In the first stage of the oxidation, A. D. Mitchell observed that the concentration of mercuric chloride appeared to have no influence on the reaction velocity except when very dil. The reaction was accelerated by the addition of hydrochloric acid. It was therefore auto-catalytic, owing to the hydrochloric acid produced The initial velocity was approximately proportional to the product of the concentrations of the hydrogen ions and the hypophosphorous acid. It was therefore concluded that the oxidation to phosphorous acid involved two successive reactions: the first, of measurable velocity, in which the mercuric chloride took no part, and the second, of relatively great velocity, in which the mercuric chloride played a part. As in the case of iodine (*vide supra*), it was found that the measurable velocity of the reaction between hypophosphorous acid and mercuric chloride, if the soln. are not too dil., is independent of the conc. of the latter, as in the analogous reaction with iodine, and is due to the re-establishment of equilibrium between hypophosphorous acid *molecules* and the hypothetical "active" form, H_5PO_3. This change is catalyzed by hydrogen ions, and the reaction is therefore autocatalytic. This is followed by a rapid reaction which can only be detected at low concentrations. The evidence is strong, but not quite conclusive that this reaction takes place between one mol of mercuric chloride (and not of its ions or possible complexes) and two mols of "active" hypophosphorous acid. R. Engel found that the precipitation of metal from **stannous salts,** and **lead salts** by hypophosphorous acid and palladium interferes with the catalytic activity of the palladium; but the mixture completely decomposes **antimony salts** at ordinary temp.; and likewise also **bismuth salts.** W. Muthmann and F. Mawrow showed that soln. of bismuth salts give a precipitate of bismuth. **Arsenic salts** give a brown coloration with hypophosphorous acid, and on that account, E. Deussen, and E. Rupp and E. Muschiol recommended calcium hypophosphite as a precipitant for arsenic in detecting that element in soln. of arsenic salts. I. M. Kolthoff, and M. Major studied the oxidation of hypophosphites by soln. of **potassium dichromate.** A. D. Mitchell indicated that the reaction with chromic acid is probably the resultant of a slow, unimolecular reaction: $H_3PO_2+Cr_2O_7''=H_3PO_3+Cr_2O_6''$, and the fast reaction: $2H_3PO_2+Cr_2O_6''+8H^{\cdot}=2H_3PO_3+2Cr^{\cdot\cdot\cdot}+4H_2O$, *vide supra.* The velocity constants vary inversely as the 7th power of the initial conc. of the chromic acid. According to A. Winkler, hypophosphorous acid and hypophosphites give a blue coloration or a blue precipitate with **ammonium molybdate;** but E. J. Millard could not obtain other than a faint coloration, if at all, with acidic, neutral, or alkaline soln. of the molybdates. He found that the addition of a small quantity of sulphurous acid renders the test a most delicate one, and one which the ordinary nitric acid soln. of ammonium molybdate answers well. Phosphates, pyrophosphates, and phosphites do not give the reaction when similarly treated. In pure soln. it is possible to detect 1 part of hypophosphorous acid in 2000. C. Ebaugh and E. F. Smith observed that the molybdic acid is reduced to the pentoxide, Mo_2O_5; and that the method is untrustworthy for quantitative analysis. O. W. Gibbs prepared complex hypophosphatomolybdates—*vide infra.* F. X. Moerk obtained colour reactions with **sodium tungstate** and hypophosphorous acid in the presence of sodium sulphite. O. W. Gibbs prepared complex hypophosphatotungstates. L. P. de St. Gilles, and I. M. Kolthoff, found that **potassium permanganate** oxidizes hypophosphorous acid completely to phosphoric acid. L. Amat found that the oxidation proceeds more quickly the more conc. the soln., the more acidic the soln., and the higher the temp.; at ordinary temp., and in dil. soln., the oxidation is incomplete. If the soln. be too hot, some permanganate may be decomposed without interaction with the hypophosphorous acid. The reaction was studied by I. M. Kolthoff. M. Major, and A. Sieverts found that reduced **iron** readily dissolves in a hot soln. of sodium hypophosphite; **ferric salts** are reduced to the ferrous state; and ferric alum reacts at the temp. of the water-bath, while phosphorous acid is not attacked after several hours. M. Major studied the reduction of iron alum by hypophosphites. A. D. Mitchell found that a considerable error is caused by the presence of hypophosphorous acid when ferrous salts are titrated by potassium dichromate. This is tentatively ascribed to the ferrous salt acting as "inductor" in the oxidation of hypophosphorous acid by chromic acid, probably in virtue of the transient formation of the quinquevalent chromium compound, which has been found by other workers also to be exceedingly reactive. He also found that finely-divided **nickel** and **cobalt** behave like palladium (*vide infra*) in oxidizing soln. of the hypophosphites, with the evolution of hydrogen. Soln. of **cobalt salts** and of **nickel salts** are not reduced by hypophosphorous acid, but the metals reduced by hydrogen oxidize cold soln. of sodium hypophosphite to phosphite. Soln. of **platinum salts** are not reduced by hypophosphites, even when boiling. A. Atterberg, and F. Loessner showed that the gradual darkening of the soln. of platinic chloride is due to the formation of platinous chloride. F. Loessner, and M. Major showed that the oxidation of the hypophosphite which occurs in the presence of finely-divided **platinum** is due to the occluded oxygen. C. A. Wurtz, F. Loessner, and A. Sieverts found soln. of **palladium salts** are reduced by hypophosphorous acid in the cold, and, according to the former, some hydrogen is given off; F. Loessner represented the reaction: $2PdSO_4+H_3PO_2+2H_2O=2Pd+H_3PO_4+2H_2SO_4$. R. Engel said that palladium precipitated from a soln. of the chloride by means of hypophosphorous acid retains a small quantity of hydrogen. The quantity of hydrogen evolved is much greater than the quantity which could be liberated from a palladium hydride. When spongy **palladium** is brought in contact with hypophosphorous acid, the latter is rapidly converted into phosphorous acid, and hydrogen is liberated. The palladium seems to retain its activity indefinitely, and 0·5 grm. of the metal decomposed the acid obtained from 500 grms. of barium hypophosphite. The reaction is not arrested by press. It is probable that the palladium removes an atom of hydrogen from the hypophosphorous acid, but quickly loses it, whilst the residue of the acid interacts with the water, combining with hydroxyl, and liberating another atom of hydrogen. The reaction was studied by F. Loessner, and M. Major—the latter represents the reaction $H_3PO_2+H_2O=H_2+H_3PO_3$. Water is necessary for the reaction; alcohol will not do. The presence of sodium hydrocarbonate favours the reaction, while alkali or sulphuric acid retards the reaction. According to A. Sieverts, even a cold soln. of sodium hypophosphite is oxidized by precipitated palladium to phosphite, and even further on boiling. Alcoholic sodium hypophosphite does not react with palladium.

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§ 15. The Hypophosphites

The hypophosphites are obtained by dissolving the bases in an aq. soln. of the acid ; by boiling phosphorus with alcoholic potash ; or by boiling phosphorus with the hydroxides of the alkalies or alkaline earths in aq. soln. Many of the hypophosphites are obtained by treating the barium salt with the sulphates of the other metals, or the calcium salt with the carbonates. The solid salts are usually stable in air. When heated, the salts of sodium, thallium, lithium, magnesium, zinc, cadmium, calcium, strontium, barium, manganese, and lead give off hydrogen and phosphine, and leave pyro- or meta-phosphates behind ; the cobalt and nickel salts form the metaphosphate and phosphide ; and the uranium salt gives a mixture of meta- and pyro-phosphates and phosphide. The hypophosphites are nearly all fairly soluble in water, and the alkali salts are also soluble in alcohol. If the aq. soln. are boiled out of contact of air, they suffer no change, but in air, they are oxidized to phosphites and phosphates ; when heated with alkalies, they form phosphites and phosphates with the evolution of hydrogen. According to C. F. Rammelsberg,[1] the hypophosphites are all decomposed by heat furnishing pyrophosphate and metaphosphate in the molar proportion 1 : 1 with the sodium and thallium salts ; 2 : 1 with the magnesium, zinc, and manganese salts ; 3 : 1 with calcium, strontium, cadmium, and cerium salts ; 4 : 1 with the lead salt ; and 6 : 1 with the barium salt. The nickel and cobalt salts yield metaphosphate and phosphide ; and the uranyl salt, pyrophosphate, metaphosphate, and phosphide.

H. Rose studied mainly the gaseous products and his work on the solid product was incomplete. C. F. Rammelsberg found that the gaseous products of the decomposition of hypophosphites being always a mixture of hydrogen and phosphine, the inflammability of the gas is of no importance, and seems to vary according to circumstances. The separation of phosphorus is due to the process itself, and does not depend on the decomposition of phosphine, for very often phosphorus appears at the beginning of the process, when the temp. is not sufficient for the decomposition of phosphine.

According to G. Polk,[2] P. Schulz, and M. Paquelin and L. Joly, there is no evidence that the hypophosphites exert the slightest toxic effect. They pass through the system unchanged. According to T. Panzer, experiments with dogs showed that calcium hypophosphite is rapidly eliminated from the system and passes unaltered into the urine. The presence of hypophosphite may be generally detected after half an hour, and no more can be found after 24 hrs. The other organs, blood, and fæces are practically free from hypophosphite. In human beings the elimination seems to take a little longer. In case of a supposed poisoning by phosphorus, inquiries should be made as to whether the person has taken any hypophosphite shortly before death ; should this be proved, the presence of phosphorous acid in the urine or intestinal canal counts for nothing. As previously indicated, the hypophosphites have been tried as explosives but without any particularly useful results. The *ferri hypophosphis*, *sodii hypophosphis*, and *calcii hypophosphis* of the pharmacopœia are respectively iron, sodium, and calcium hypophosphites.

P. L. Dulong,[3] C. F. Rammelsberg, and C. A. Wurtz prepared **ammonium hypophosphite,** $(NH_4)H_2PO_2$. It is obtained by treating barium hypophosphite with ammonium sulphate, evaporating the filtrate to dryness, and crystallizing the product from its soln. in hot water or alcohol. A. Michaelis and K. von Arend treated the acid or the calcium or barium salt with ammonium carbonate in excess, and evaporated the filtrate as before. The salt was analyzed by C. A. Wurtz, and A. Michaelis and K. von Arend. C. F. Rammelsberg measured the crystal angles, and J. Beckenkamp gave for the axial ratios of the rhombic bipyramidal crystals $a:b:c=0·5276:1:1·5137$; and C. F. Rammelsberg, $0·339:1:0·665$. The large, tabular crystals were found by C. A. Wurtz to melt at about 200° without loss of water, but at 240°, water and spontaneously inflammable phosphine are given off, and, according to H. Rose, ammonia is also evolved. C. F. Rammelsberg represented the reaction : $7(NH_4)H_2PO_2=H_4P_2O_7+2HPO_3+H_2O+7NH_3+3PH_3+2H_2$. The crystals are less deliquescent than those of the potassium salt. H. Stamm found that the conc. aq. soln. is not changed by the introduction of ammonia. P. L. Dulong found that salt to be freely soluble in alcohol. A. Michaelis and K. von Arend obtained phosphorus tetritoxide by treating the salt with acetic anhydride.

According to A. P. Sabanéeff, **hydroxylamine hypophosphite,** $(NH_3OH)H_2PO_2$, is formed when the barium salt is treated with hydroxylamine hydrosulphate only in an atm. of carbon dioxide because the aq. soln. of the salt is so easily oxidized on exposure to air ; the filtered soln. is evaporated for crystallization without raising the temp. K. A. Hofmann and V. Kohlschütter mixed potassium hypophosphite and hydroxylamine chloride so as to keep the soln. acidic; the product was extracted with hot absolute alcohol, and precipitated from that soln. with ether. The acicular crystals are very hygroscopic ; and they can be preserved in suitable vessels without change. A. P. Sabanéeff found that when the salt is heated, it begins to decompose at about 60°, and fusion occurs at about 92°, forming a transparent mass which detonates at a still higher temp. The salt is freely soluble in water ; and the aq. soln. exhibits the reactions of both hydroxylamine and hypophosphorous acid ; it reduces cold, alkaline soln. of copper salts, and gives no precipitate with barium chloride. The salt is isomeric with ammonium phosphite.

C. F. Rammelsberg prepared **lithium hypophosphite,** $LiH_2PO_2.H_2O$, by double decomposition with soln. of the barium salt and of lithium sulphate. The soln. yields small, colourless, transparent, prismatic crystals belonging to the monoclinic system, and with the axial ratios: $a:b:c=0{\cdot}623:1:1{\cdot}952$, and $\beta=79°\ 52'$. The salt is anhydrous after drying at 200°; if confined over conc. sulphuric acid, it loses one-third of its water of crystallization; and when heated, it decomposes: $9LiH_2PO_2=2Li_4P_2O_7+LiPO_3+4PH_3+2H_2+H_2O$. The salt is freely soluble in water; and when heated with nitric acid, and evaporated, lithium metaphosphate is formed. P. L. Dulong, and H. Rose prepared **sodium hypophosphite,** $NaH_2PO_2.H_2O$. It can be obtained by double decomposition with the calcium salt and sodium carbonate, and evaporating the alcoholic soln. in vacuo. C. F. Rammelsberg prepared it by double decomposition with the barium salt and sodium carbonate, or by treating the acid with sodium carbonate. The aq. soln. can be evaporated to dryness over conc. sulphuric acid. W. Engelhardt described the preparation of the salt. L. C. Marquart, and H. Trommsdorff noted explosions may occur when the soln. is evaporated on the water-bath, or sand-bath.

The commercial salt can be purified by converting it into the barium salt, which is then treated with sodium sulphate. The filtrate is then treated with alcohol and ether to precipitate any calcium hypophosphite which may be present. The filtrate was then evaporated for the sodium salt. J. Beckenkamp found that the monoclinic prisms of the hydrated salt have the axial ratios $a:b:c=0{\cdot}8199:1:2{\cdot}2320$, and $\beta=123°\ 16'$. The salt was found by C. F. Rammelsberg to lose about half its water of crystallization, over conc. sulphuric acid; and at 200° it is almost anhydrous. When heated to a higher temp. H. Rose noted that spontaneously inflammable phosphine is emitted; and C. F. Rammelsberg represented the reaction: $5NaH_2PO_2=Na_4P_2O_7+NaPO_3+2PH_3+2H_2$. The salt is deliquescent in air, and, added H. Rose, rather less so than the potassium salt. J. Thomsen measured the heat of formation from base and acid (*q.v.*). S. Arrhenius found the heat of ionization to be —196 cals. at 35°. P. L. Dulong found the salt to be freely soluble in water, and in alcohol; and when evaporated with nitric acid, C. F. Rammelsberg obtained sodium metaphosphate. According to A. Cavazzi, mixtures of hypophosphites and nitrates are powerful explosives: $NaH_2PO_2+2NaNO_3=Na_3PO_4+H_2O+NO_2+NO$; and A. Berg and L. Cari-Mantrand obtained explosives from mixtures of hypophosphites and chlorates. A mixture of equal parts of barium hypophosphite and potassium chlorate, previously dried at 100°, burns in the open air with great rapidity, producing a feeble report; but when at all confined, as, for instance, in a screw of paper, a sharp detonation results. An electric spark readily fires the mixture; and it is, moreover, very sensitive to shocks and friction, so that great care must be observed in its preparation. A mixture of the explosive with magnesium powder burns very rapidly and with dazzling brilliancy; and as no special contrivance is needed for its combustion, it might be employed as a flashlight for photographic purposes. As the powder is so readily fired by an electric spark, it might advantageously replace mercuric fulminate. It is much cheaper than the latter, and its two components, which need be mixed only when required, are perfectly harmless when separate. A mixture of syrupy sodium hypophosphite and powdered sodium chlorate in some respects resembles nitroglycerol. A drop when heated on metal foil liquefies, boils, and finally, when quite dry, explodes with great violence, generally perforating or deeply indenting the foil. Trials with other hypophosphites did not yield good results. A. Gutmann observed no reaction between sodium hypophosphite and a cold or boiling soln. of sodium thiosulphate—this appears strange in view of the reducing action of the hypophosphite in acidic soln. Aq. soln. of sodium hypophosphite are oxidized under the influence of spongy palladium or palladium black, but not by the wire or foil. The reaction with the greater velocity is symbolized: $NaH_2PO_2+H_2O=NaH_2PO_3+H_2$, so that hydrogen is evolved during the oxidation. The oxidation to phosphate, $NaH_2PO_3+H_2O=NaH_2PO_4+H_2$, proceeds by a slower reaction. N. Bakh studied the poisoning of the catalyst

—palladium—in the reaction, $NaH_2PO_2+H_2O=NaH_2PO_3+H_2$, where the progress of the reaction is measured by the vol. of hydrogen evolved, and the cessation of the evolution of hydrogen shows that complete poisoning has occurred. Each mol of palladous chloride requires 1·75 mols of potassium cyanide, 1·5 mols of thiourea, one mol of mercuric chloride, or over 10 mols of quinine hydrochloride. The poisoning is due partly to the formation of a compound of palladous chloride with the poison which cannot be reduced by the hypophosphite, and partly to the adsorption of the poison by palladium black which cannot then act as a catalyst. With colloidal palladium, the poisoning effect is due to the binding of the mols of the poison on the surface of the palladium particles. H. Stamm found that the sat. aq. soln. gives a precipitate when ammonia is added.

P. L. Dulong prepared **potassium hypophosphite,** KH_2PO_2, in 1816, but T. von Grotthus, and L. Sementini obtained it from the soln. obtained by boiling alcoholic potash-lye with phosphorus, but they mistook the product for a phosphide. H. Rose made it by double decomposition with the calcium salt and potassium carbonate, and C. A. Wurtz, with the barium salt and potassium sulphate. In both cases the filtrate was evaporated to dryness, the product extracted with alcohol, and the alcoholic soln. evaporated in vacuo. H. Rose extracted it from the soln. obtained by boiling phosphorus with potash-lye. The liquid was left to evaporate slowly in air so that the potassium hydroxide may be converted into carbonate. The residue was leached with alcohol, and the alcoholic soln. evaporated in vacuo. The liquid obtained by boiling phosphorus with alcoholic potash-lye can be used; this is decanted, and, if necessary, it is mixed with alcohol to redissolve the salt, which may have crystallized out. Powdered potassium hydrocarbonate is added to convert the hydroxide into carbonate. The soln. is then treated as before. P. L. Dulong found the salt to be more deliquescent than calcium chloride. C. A. Wurtz said that the crystals are hexagonal plates which do not lose weight at 100°, but when heated in a closed vessel give off spontaneously inflammable phosphine, and leave potassium pyrophosphate. C. F. Rammelsberg represented the reaction: $5KH_2PO_2=K_4P_2O_2+KPO_3+2PH_3+2H_2$. L. Sementini said that when the salt is heated, it burns in air with a yellow flame; and detonates vigorously when evaporated with nitric acid. H. Rose found that when boiled with potash-lye, hydrogen is given off and potassium phosphite is formed, and in conc. soln., potassium phosphate. C. A. Wurtz found the salt to be freely soluble in aq. alcohol, less soluble in absolute alcohol, and insoluble in ether. V. Bayerle found that the polarization curve of a soln. of potassium hypophosphite indicates that the soln. is decomposed at the same temp. as that at which potassium ions are deposited; this is taken to show that phosphorus ions are not split off. According to K. A. Hofmann and V. Kohlschütter, **potassium hydroxylamine hypophosphite,** $K_2(NH_2OH)_3(H_2PO_2)_2$, is obtained by neutralizing phosphorous acid with ammonia, then adding four times the quantity of ammonia and two mol. parts of hydroxylamine hydrochloride to one part of the acid; after remaining one hour, the soln. is precipitated with alcohol and the product recrystallized from absolute alcohol. It is also obtained by heating normal ammonium phosphite with a soln. of hydroxylamine hydrochloride in absolute ethyl alcohol and dissolving out the excess of hydroxylamine hydrochloride from the product by warming it with methyl alcohol. It crystallizes in slender, white needles, and at once reduces Fehling's soln. and ammoniacal silver nitrate.

According to H. Rose, the blue soln. of cupric hydroxide in cold hypophosphorous acid may remain unaltered for a long time; and if very dil., it may even be heated without decomposition. If the soln. be evaporated in vacuo at a low temp., the copper is completely reduced as soon as the liquid is highly concentrated C. A. Wurtz found that the soln. obtained by double decomposition of barium hypophosphite and copper sulphate at about 60° precipitates copper hydride—*vide supra.* Once blue crystals of **copper hypophosphite,** $Cu(H_2PO_2)_2$, were obtained; they decomposed abruptly at 65°. According to R. Engel, this salt may be obtained by mixing soln. of barium hypophosphite and cupric sulphate, and adding alcohol to the clear liquor. It forms a brilliant, white precipitate of the composition $Cu(H_2PO_2)_2$, and is somewhat stable both in the solid state and in soln. The solid explodes suddenly at about 90° ; a dil. soln. can be boiled without decomposing. Precipitated palladium decomposes cupric hypophosphite soln. in accordance with the following equation: $Cu(H_2PO_2)_2+2H_2O=Cu+2H_3PO_3+H_2$, and copper hydride is not formed. If, however, an aq. soln. of the salt is boiled, brown cuprous hydride is first precipiated and rapidly splits up into hydrogen and copper. In the first phase of the reaction, hypophosphorous acid is formed, but is slowly oxidized by the copper at about 100°, whereas with palladium this oxidation takes place at the ordinary temp. G. T. Morgan and F. H. Burstall prepared **copper bisethylenediaminohypophosphite,** $[Cu(en)_2](H_2PO_2)_2$, by adding a soln. of barium hypophosphite to onc of copper sulphate and ethylenediamine, and crystallizing the filtrate. The hygroscopic product decomposes rapidly at 115°. A. Gutbier found that dil. hypophosphorous acid gives a white precipitate of **silver hypophosphite** when added to soln. of silver nitrate; if warmed, the salt decomposes rapidly with the separation of silver. No gold hypophosphite has been made—*vide supra* for the action of hypophosphorous acid on the salts of copper, silver, and gold.

H. Rose prepared **calcium hypophosphite,** $Ca(H_2PO_2)_2$, by boiling phosphorus with milk of lime, replacing the water which evaporates from time to time. When the smell of phosphine is no longer perceptible, the filtrate is freed from an excess of lime by the passage of carbon dioxide, and gently warming the mixture to decompose any hydrocarbonate; the filtered soln. is evaporated either in vacuo over conc. sulphuric acid, or in air at a gentle heat—in the latter case, some calcium phosphate is formed—*vide supra*, hypophosphorous acid. C. A. Wurtz, G. Janssen, W. Engelhardt, and L. Berlandt employed a similar process. J. Bachmann decomposed calcium phosphide by boiling water, and after digesting the mixture for some time extracted the hypophosphite as in H. Rose's process. J. F. Martenson employed a similar process. Analyses of the salt were made by H. Rose, C. A. Wurtz, J. Bachmann, and C. F. Rammelsberg. The salt is anhydrous. H. Rose said that the crystals are colourless, rectangular prisms with terminal faces obliquely inclined to the two broad lateral faces; C. F. Rammelsberg gave for the axial ratios of the monoclinic prisms $a:b:c=0\cdot8693:1:1\cdot200$, and $\beta=75° 12'$; and J. Schabus, $1\cdot1963:1:1\cdot3854$, and $\beta=104° 48'$. The crystals became tabular by the extension of the (001)-face; twinning occurs about the (001)-face; and the cleavage on the (001)-face is perfect. The plates are transparent and flexible, and undergo no change on exposure to air. According to J. Bachmann, the crystals have a nauseous, bitter taste. C. A. Wurtz found that the crystals do not lose any water at 100°, but, according to H. Rose, the crystals decrepitate when heated to redness in a retort, and give off first water, then spontaneously inflammable phosphine; C. F. Rammelsberg represented the reaction: $7Ca(H_2PO_2)_2=3Ca_2P_2O_7+Ca(PO_3)_2+6PH_3+4H_2+H_2O$. A. Michaelis gave a similar equation. When heated with nitric acid, the crystals form calcium metaphosphate; and J. Bachmann found that the salt inflames when a small quantity of fuming nitric acid is poured on it; it detonates when admixed with potassium chlorate and quartz; and instantly reduces silver nitrate. H. Rose said that with boiling potash-lye it forms phosphite, but no phosphate; and that the salt is insoluble in conc. alcohol, and sparingly soluble in dil. alcohol. C. A. Wurtz, and H. Rose found that 100 parts of water dissolve 16·7 parts of salt at ordinary temp., and not much more in hot water. G. Janssen said that a soln. of calcium hypophosphite forms carbonate and phosphate when exposed to air; that sulphur, selenium, and tellurium also decompose it into phosphite, then into phosphate, with formation of calcium sulphide, selenide, or telluride respectively. Boron, silicon, and carbon decompose it by heat; calcium borate, silicate, or carbonate is formed, and phosphorus evolved as vapour. Hydrogen decomposes it into phosphate and phosphine. Hydrochloric, hydriodic, hydrobromic, and hydrofluoric acids decompose it into phosphate, phosphine, and a haloid salt. Nitric acid converts it into phosphate, nitrogen peroxide being evolved. The alkaline bases decompose it into phosphate and phosphide. The alkaline carbonates when boiling, and the alkaline sulphates in the cold, transform it into an alkaline hypophosphite and calcium carbonate or sulphate. It precipitates metallic gold from its soln. In a soln. of silver nitrate it produces a white precipitate, which rapidly turns brown; if the hypophosphite be added in excess in the cold, it reduces the silver to the metallic state after some time; by the aid of heat the reduction is more rapid. In a dil. soln. of mercuric chloride, it produces a crystalline precipitate of mercurous chloride. If added in excess it reduces the mercury to the metallic state. From a soln. of copper sulphate it precipitates the oxide, which a continued ebullition reduces to the metallic state.

P. L. Dulong made **strontium hypophosphite,** $Sr(H_2PO_2)_2$, by adding the phosphide to water, and evaporating the filtered liquid to the crystallizing point. H. Rose boiled phosphorus with strontia-water until no more phosphine was evolved; the soln. was filtered from the phosphate produced at the same time, evaporated over sulphuric acid in vacuo; and the residue dissolved in hot water and cooled for crystallization. C. A. Wurtz employed a similar process. Instead of strontia-water, a soln. of strontium sulphide, which generally contains more sulphur than corresponds with the monosulphide, can be used; it acts in the cold. The phosphorus absorbs the excess of sulphur, forming a compound which is broken down by water into hydrogen sulphide and hypophosphorous acid. If heat be applied, there is evolved a mixture of spontaneously inflammable phosphine, hydrogen, and, maybe, a little hydrogen sulphide. The soln. contains strontium hypophosphite, and strontium hydrosulphide which is not decomposed by the phosphorus. The hydrosulphide is decomposed either by lead carbonate or dil. sulphuric acid. The filtered liquid is then evaporated for the strontium salt as before. C. F. Rammelsberg made the salt by dissolving strontium carbonate in hypophosphorous acid, and evaporating the liquor at ordinary temp. According to C. A. Wurtz, the salt appears in masses of tabular crystals and plates which do not lose weight at 100°; C. F. Rammelsberg said the salt is monohydrated, and becomes anhydrous at 200°. H. Rose found that when heated to a higher temp. it gives off spontaneously inflammable phosphine, and C. F. Rammelsberg, and A. Michaelis represent the reaction by an equation similar to that employed for the calcium salt. P. L. Dulong said that the salt is freely soluble in water; and C. A. Wurtz, soluble in alcohol. P. L. Dulong, H. Rose, C. F. Rammelsberg, and C. A. Wurtz prepared **barium hypophosphite,** $Ba(H_2PO_2)_2.H_2O$, by processes similar to those which they employed for the strontium salt. H. Rose obtained crystals of the monohydrate by cooling the hot aq. soln.; and C. A. Wurtz, by adding alcohol to the aq. soln. The crystals are white or colourless needles or prisms with a pearly lustre. They belong to the monoclinic system, and, according to C. F. Rammelsberg, have the axial ratios $a:b:c=1·575:1:1·200$, and $\beta=79°\ 40'$. H. Töpsöe gave 2·0017 : 1 : 1·5760, and $\beta=99°\ 33'$. Twinning about the (101)-face frequently occurs. According to H. G. F. Schröder, the sp. gr. is 2·839–2·911; and, according to F. W. Clarke, 2·8718 at 10°; 2·8971 at 17°; 2·780 at 21·6°; and 2·775 at 23·3°. P. Walden gave for the eq. electrical conductivity, λ, for soln. with a gram-equivalent in v litres:

v .	32	64	128	256	512	1024	∞
λ .	78·7	84·1	88·2	91·8	94·6	97·3	105·3

G. Bredig made observations on this subject. The dry salt, said C. A. Wurtz, is stable in air; and no loss in weight over conc. sulphuric acid was observed by C. F. Rammelsberg. C. A. Wurtz said the salt becomes anhydrous at 100°; and C. F. Rammelsberg, at 100°–150°. H. Rose said that when the salt is heated, water is first evolved, and then spontaneously inflammable phosphine. The residue has a reddish colour, presumably owing to the formation of a little red phosphorus,

C. F. Rammelsberg represented the reaction: $13Ba(H_2PO_2)_2=6Ba_2P_2O_7+Ba(PO_3)_2+12PH_3+4H_2+4H_2O$. J. Thomsen gave 0·29 Cal. for the heat of soln. of a mol of the monohydrate in 800 mols of water; and for the heat of neutralization of the acid with $Ba(OH)_2$aq., 30·92 Cals. C. A. Wurtz said that 100 parts of water at ordinary temp. dissolve 28·5 parts of salt; and 100 parts of boiling water, 33·3 parts of salt; it is insoluble in alcohol; and when heated with potash-lye, barium phosphite is precipitated—the reaction is symbolized: $Ba(H_2PO_2)_2+2KOH=BaHPO_3+K_2HPO_3+2H_2$. By heating the crystals of the salt with nitric acid, C. F. Rammelsberg obtained barium metaphosphate.

H. Rose evaporated in vacuo a soln. of beryllium hydroxide in phosphoric acid, and obtained a sticky substance, presumably **beryllium hypophosphite,** $Be(H_2PO_2)_2$, which dried to a hard mass with a conchoidal fracture. B. Bleyer and B. Müller mixed a mol. of beryllium sulphate and barium hypophosphite in aq. soln.; evaporated the filtrate over conc. sulphuric acid and obtained a glassy residue with the composition just indicated. H. Rose obtained **magnesium hypophosphite,** $Mg(H_2PO_2)_2.6H_2O$, by boiling the calcium salt with magnesium oxalate and water; and C. A. Wurtz, by the double decomposition of the barium salt and magnesium sulphate. H. Rose, and C. F. Rammelsberg wrongly described the crystals as octahedrons with the faces of a cube. J. Beckenkamp showed that the crystals are tetragonal bipyramids, with the axial ratio $a:c=1:0·9878$. The birefringence is feeble and positive. F. W. Clarke gave for the sp. gr. 1·5886 at 12·5°, and 1·5681 at 14·5°. H. Rose found that the crystals effloresce in air, and when heated to 100°, C. A. Wurtz found that they lost five-sixths of their water of crystallization, and the remainder at 180°. When heated to a higher temp., H. Rose found that phosphine is emitted, and a reddish mass remains. C. F. Rammelsberg represented the reaction: $5Mg(H_2PO_2)_2=2Mg_2P_2O_7+Mg(PO_3)_2+4PH_3+4H_2$. When the crystals are heated with nitric acid, H. Rose found that magnesium metaphosphate is formed. By dissolving zinc carbonate in hypophosphorous acid, and evaporating the soln. in vacuo, H. Rose obtained indistinct crystals. The salt is obtained by double decomposition in aq. soln.; and C. A. Wurtz found that if evaporated at ordinary temp., crystals of hexahydrated **zinc hypophosphite,** $Zn(H_2PO_2)_2.6H_2O$, isomorphous with the magnesium salt are formed; and by evaporating the hot soln., the rhombohedral crystals, dried at 100°, are monohydrated. F. W. Clarke gave 2·016 for the sp. gr. of the hexahydrate at 12·5°; and 2·014 at 19·5°. H. Rose and C. F. Rammelsberg found that the salt is decomposed by heat as in the case of the magnesium salt. H. Rose obtained **cadmium hypophosphite,** by evaporating in vacuo a soln. of hypophosphorous acid sat. with cadmium carbonate. The cadmium salt behaves like the zinc salt when heated. H. Rose obtained indications of the existence of a complex salt *calcium cadmium hypophosphite* by evaporating the filtrate from the liquor obtained by boiling cadmium oxalate, calcium hypophosphite, and water. The **mercury hypophosphites** have not been prepared. H. Rose found that mercuric chloride is reduced to mercurous chloride and to mercury when treated with hypophosphorous acid. S. Hada observed that **mercurous nitratohypophosphite,** $Hg(H_2PO_2).Hg(NO_3).H_2O$, is precipitated on adding a soln. of potassium or barium hypophosphite to a soln. of mercuric or mercurous nitrate, free from nitrous acid, but the mercury soln. must not be too dil., and as free from acid as possible; care must also be taken to avoid using excess of the hypophosphite. The compound is not obtained when the mercury nitrate soln. is added to the hypophosphite, or if too much of the latter is added to the mercury nitrate, as in either case the double salt is at once decomposed. Since the formation of the salt from mercuric nitrate necessarily involves the oxidation and waste of much of the hypophosphite, and also yields a mother-liquor which acts strongly on the precipitate, mercurous nitrate should be used; moreover, potassium hypophosphite is preferable to the barium salt, as with the latter the precipitate is liable to contain barium apparently as nitrate. As the white precipitate obtained on adding potassium hypophosphite to an excess of mercurous nitrate is slowly decomposed when left in contact with the mother-liquor, it must be quickly collected and drained on a tile, without previous washing. The *mercurous nitratohypophosphite* thus obtained is unstable when moist, although when dry it decomposes but slowly, becoming grey in the course of time. It is a white, micaceous powder, slightly soluble in water, by which it is soon decomposed with separation of mercury; it loses its water of crystallization in a vacuum desiccator, but undergoes scarcely any decomposition, even when kept for some time. When heated, it turns grey above 90°, and explodes a little above 100°, yielding mercury and nitrous vapours; it also explodes if touched with a hot wire. With hydrochloric acid, it first gives mercurous chloride and then metallic mercury, whilst hot, strong nitric acid dissolves it completely with the evolution of nitrous fumes. Sodium chloride converts it into mercurous chloride and sodium hypophosphite, which only very slowly react, yielding metallic mercury. Potassium hydroxide blackens it, probably from formation of mercurous oxide.

H. Rose reported **aluminium hypophosphite** to be formed by dissolving aluminium hydroxide in cold hypophosphorous acid, and evaporating the filtered soln. in vacuo. The viscid product dries to a hard mass with a conchoidal fracture, and is not deliquescent. When heated in a retort, phosphine is evolved and a reddish substance remains. C. F. Rammelsberg prepared **thallous hypophosphite,** TlH_2PO_2, by the double decomposition of the barium salt with thallous sulphate. The prismatic crystals are anhydrous, and belong to the rhombic system with the axial ratios $a : b : c = 0{\cdot}786 : 1 : 0{\cdot}805$. They melt at 150° and are decomposed by heat: $5TlH_2PO_2 = Tl_4P_2O_7 + TlPO_3 + 2PH_3 + 2H_2$. According to O. Hauser and H. Herzfeld, **zirconium hypophosphite,** $Zr(H_2PO_2)_4.H_2O$, is obtained by adding hypophosphorous acid to a soln. of zirconium nitrate until the precipitate has completely redissolved, and then adding alcohol. It forms colourless, highly refracting crystals, which become deep violet very rapidly in direct sunlight, or in the course of several weeks in diffused daylight, without any other perceptible change. C. F. Rammelsberg prepared **cerium hypophosphite,** $Ce(H_2PO_2)_3.H_2O$, in thin prismatic crystals, from the soln. obtained by decomposing the barium salt with cerium sulphate. The salt decomposes when heated yielding products like those with the calcium and strontium salts. O. Kauffmann reported **thorium hypophosphite,** $Th(H_2PO_2)_4.H_2O$, to be found by mixing a cold soln. of the sodium salt with one of thorium nitrate. The salt is washed free from nitric acid, and dried on a porous tile; the anhydrous salt was obtained by adding thorium nitrate to a soln. of hypophosphorous acid. The salt is insoluble in water, but very soluble in conc. mineral acids. When the soln. in conc. hydrochloric acid is evaporated over a flame, aggregates of crystals of **thorium hydroxytrihypophosphite,** $Th(OH)(H_2PO_2)_3.4H_2O$, are formed. The crystals are insoluble in water, but soluble in dil. hydrochloric acid.

The *tin hypophosphites* have not been prepared; A. Terni and C. Padovani found that when solid or a conc. soln. of stannous chloride is added to a conc. soln. of sodium hypophosphite, there is a voluminous white precipitate of **stannic chlorohypophosphite,** $SnCl_4.Sn(H_2PO_2)_4.3H_2O$, which is strongly reducing. This compound is dehydrated at 140°, and, at 190°, it decomposes, with a characteristic reddening and evolution of phosphine. If the heating is stopped immediately, and the mass extracted with conc. hydrochloric acid, the composition of the bright red residue approximates to P_4O. T. von Grotthus, H. Rose, and C. A. Wurtz made observations on **lead hypophosphite,** $Pb(H_2PO_2)_2$. H. Rose obtained it by saturating a hot aq. soln. of hypophosphorous acid with lead oxide. If the soln. is heated, lead is precipitated. C. A. Wurtz treated the acid with freshly precipitated lead carbonate. In both cases, the filtered soln. was evaporated. E. von Herz treated a hot sat. soln. of the calcium salt with a hot sat. soln. of lead nitrate, when crystals of lead hypophosphite separated on cooling. According to H. Rose, and C. A. Wurtz, the small rhombic prisms have a feeble acidic reaction towards litmus, and they lose no water at 100°. When heated in a retort, phosphine is evolved; and C. F. Rammelsberg represented the reaction: $9Pb(H_2PO_2)_2 = 4Pb_2P_2O_7 + Pb(PO_3)_2 + 8PH_3 + 4H_2 + 2H_2O$. W. Ipatieff and co-workers found that lead hypophosphite gives phosphorous acid, lead oxide, and black phosphorus when it is heated in a current of hydrogen. H. Rose found the salt to be sparingly soluble in cold water, but more readily soluble in hot water; it is not soluble in alcohol, and alcohol precipitates the salt from its aq. soln. in pearly scales. The aq. soln. is not decomposed by boiling. Aq. ammonia in excess precipitates what might be an impure basic salt. H. Rose believed that an excess of lead oxide formed a basic salt; C. A. Wurtz, lead phosphite. E. von Herz prepared highly explosive **lead nitratohypophosphite,** $Pb(NO_3)_2.Pb(H_2PO_2)_2$, or $Pb(NO_3)(H_2PO_2)$, by adding a hot saturated soln. of lead nitrate (331 grms.) to a boiling saturated soln. of calcium hypophosphite (170 grms.), and cooling the mixture rapidly with efficient stirring, when white, crystalline lead hypophosphite separates. Two hundred and fifty grms. of the latter are added with stirring to a boiling soln. of lead nitrate (500 grms.) in water (1·5 litres), and rapidly cooled. Its rate of detonation is greater than that of mercury fulminate and approximately equal to that of lead azide. Its small energy content, or the relatively small volume of gas liberated by its decomposition (117 litres per kilo., as contrasted with 230 litres with lead azide and 314 litres with mercury fulminate), inhibits its use as initial explosive in the usual amount of charge. Its suitable sensitiveness and detonation point, its great stability, and the high temperature of its flame render it very appropriate for percussion-fuse compositions. The double compound, dried at 40°–50°, is practically useful only when it is obtained as a heavy, granular, crystalline powder; it is less suitable in the form of needles or as a felted, voluminous mass.

S. Hada prepared **bismuth hypophosphite,** $Bi(H_2PO_2)_3.H_2O$, by mixing a soln. of bismuth nitrate, free from any unnecessary excess of nitric acid, with barium or potassium hypophosphite, avoiding excess of bismuth nitrate, as the salt is soluble in it. The bismuth hypophosphite, which is precipitated as a white crystalline powder, slowly decomposes in contact with the mother-liquor, but, if collected at once and dried on a porous tile, it can be preserved for days unchanged. L. Vanino and F. Hartl obtained it by adding hypophosphorous acid or its sodium salt to an aq. soln. of bismuth nitrate and mannitol. The white, crystalline precipitate decomposed slowly when dry; but more quickly when moist, giving bismuth. S. Hada found that bismuth hypophosphite decomposes very readily when heated, becoming black and giving off phosphine at temperatures only a little above 100°. At a stronger heat, metallic globules of bismuth and bismuth phosphate are obtained: $3Bi(H_2PO_2)_3 = 2Bi + Bi(PO_3)_3 + 6P + 9H_2O$. This hypophosphite is noticeable for yielding metal instead of phosphide.

C. A. Wurtz reported **chromium hydroxydihypophosphite,** $2Cr(OH)(H_2PO_2)_2.3H_2O$, to be formed by mixing soln. of the barium salt and chromic sulphate, and evaporating the green filtrate. The dark green, amorphous product decomposes at 200°, and is then no longer soluble in water or dil. acids. According to F. Mawrow and J. Zoneff, **chromium hypophosphite,** $Cr(H_2PO_2)_3.2H_2O$, is formed when a soln. of freshly precipitated chromium hydroxide in hypophosphorous acid yields a green mass on evaporation on the water-bath, which may be washed with water and dried over sulphuric acid. Soln. of potassium hypophosphite and chromium alum give first a deposit of potassium sulphate, and the soln. yields on further evaporation a gummy mass, from which it has not been possible to obtain a definite salt. For the action of hypophosphorous acid on molybdenum salts, *vide supra.* According to F. Mawrow, when hypophosphorous acid is added to a soln. of ammonium molybdate in conc. hydrochloric acid, a bluish-green soln. is produced and a violet deposit of **molybdenum oxyhypophosphite,** $Mo_5O_8(H_3PO_2)_7,3H_2O$, with a coppery lustre obtained. This deposit is soluble in cold water, giving a green soln. which, on exposure to air, becomes blue. It is decomposed by alkali-lye, forming a green precipitate. It is soluble in conc. sulphuric acid with a blue colour, and on dilution a yellowish-brown precipitate is formed. Heated on platinum foil, it explodes and leaves a grey residue. On heating an aqueous soln. of this, it becomes blue, and on evaporating at 90°–95°, a blue residue is obtained which is soluble in water or alcohol with a blue colour and explodes when heated. Its composition is represented by $Mo_5O_{13}(H_3PO_2)_8,H_2O$. Both these compounds are strong reducing agents, indicating that the phosphorus is present in the condition of hypophosphorous acid. It is doubtful if the formulæ given are correct, but it is certain that the substances are not compounds of molybdic acid, but of a lower oxide of molybdenum. The blue soln. gives characteristic precipitates with salts of ammonium, lead, and bismuth. F. Mawrow and N. Nikoloff said that the blue compound obtained by boiling the violet compound has the composition **molybdosic hypophosphite,** $Mo_5O_{14}.6H_3PO_2.4H_2O$, or $Mo_2O_5.3MoO_3.6H_3PO_2.4H_2O$. Its soln. gives a blue precipitate of **ammonium hypophosphitomolybditomolybdate,** $(NH_4)_2O.Mo_2O_5.5MoO_3.2H_3PO_2.4H_2O$, when treated with ammonium chloride; the precipitate with a sodium salt is **sodium hypophosphitomolybditomolybdate,** $Na_2O.Mo_2O_5.5MoO_3.3H_3PO_2.4H_2O$; with cobaltous chloride, **cobaltous hypophosphitomolybditomolybdate,** $CoO.Mo_2O_5.5MoO_3.2H_3PO_2.7H_2O$; and with lead nitrate, the **lead hypophosphitomolybditomolybdate** is mixed with lead hypophosphite. Only **barium hypophosphitomolybdate,** $BaO.Mo_7O_{20}(H_3PO_2,)_3.12H_2O$, has been examined. O. W. Gibbs reported **ammonium hypophosphitomolybdate,** $2(NH_4)_2O.8MoO_3.2H_3PO_2.2H_2O$, to be formed on mixing $(NH_4)_6Mo_7O_{24}$ with hypophosphorous acid, and then hydrochloric acid. The crystalline salt was washed with cold water. The colourless prismatic crystals are easily soluble in hot water. W. Weinberg obtained the ammonium hypophosphitomolybdate, $(NH_4)_2H.PO_2.4MoO_3.3{\cdot}5H_2O$, by mixing sodium hypophosphite and ammonium molybdate in as little water as possible, and adding hydrochloric acid. He also obtained **sodium hypophosphitomolybdate,** and **potassium hypophosphitomolybdate,** as well as the guanidinium salt. O. W. Gibbs reported **potassium hypophosphitotungstate,** $4K_2O.18WO_3.6H_3PO_2.7H_2O$, to be formed by the action of a conc. soln. of hypophosphorous acid on sodium paratungstate, dissolving the yellow product in water, and treating it with a soln. of potassium bromide. The colourless crystals are decomposed by heat. The salt is soluble in hot water, but the soln. becomes turbid, and effervesces when an alkali carbonate is added; with silver nitrate, a white precipitate of **silver hypophosphitotungstate** is formed which blackens when the soln. is hot; barium chloride gives a white precipitate of **barium hypophosphitotungstate**; and mercurous nitrate a white precipitate of **mercurous hypophosphitotungstate,** which becomes dirty yellow when the liquid is warmed.

According to V. Kohlschütter and H. Rossi, *uranium hypophosphite* has not been investigated, but M. Lobanoff prepared **uranium hypophosphite,** $U(H_2PO_2)_4$, and **uranium hydrohypophosphite,** $U(H_2PO_2)_4.H_3PO_2$, by adding the correct proportions of the acid to acidic soln. of uranic sulphate. According to A. Rosenheim and G. Trewendt, **uranyl hypophosphite,** $UO_2(H_2PO_2)_2$, is obtained in microcrystalline, yellow prisms, by agitating soln. of a mol of uranyl nitrate and 4 mols of sodium hypophosphite. The salt is almost insoluble in water, but readily soluble in excess of a soln. of either uranyl nitrate or sodium hypophosphite. They also prepared a yellow *trihydrate;* and C. F. Rammelsberg prepared the *monohydrate,* $(UO_2)(H_2PO_2)_2.H_2O$. Freshly precipitated ammonium uranate is transformed in an aq. soln. of hypophosphorous acid into the crystalline salt, which is very sparingly soluble in water. The water of crystallization is lost between 100° and 200°; and at a higher temp., it decomposes with the evolution of hydrogen and a detonation. Traces of phosphorus and phosphine are formed, and a grey residue with the composition: UP_2O_6, which is considered to be a mixture of pyrophosphate, metaphosphate, and phosphide. The main reaction is symbolized: $(UO_2)(H_2PO_2)_2{=}U(PO_3)_2{+}2H_2$. When the uranyl hypophosphite is evaporated with nitric acid, C. F. Rammelsberg found that **uranyl metaphosphate**, $(UO_2)(PO_3)_2$, is produced. A. Rosenheim and G. Trewendt observed that if uranyl hypophosphite be treated with a soln. of 4 mols of sodium hypophosphite, it forms slender, pale yellow needles of **sodium diuranyl pentahypophosphite**, $Na[(UO_2)_2(H_2PO_2)_5].4\frac{1}{2}H_2O$, or the *hexahydrate;* the corresponding **potassium diuranyl pentahypophosphite** forms yellow crusts; **ammonium diuranyl pentahypophosphite**, pale yellow leaflets; and the *guanidinium* salt, aggregates of needles. If uranyl hypophosphite be treated with 6 to 8 mols of sodium hypophosphite, it forms **sodium uranyl dihypophosphite**, $Na[(UO_2)(H_2PO_2)_2].3{\cdot}5H_2O$, in large, rectangular plates; the *pentahydrate* was also prepared. Attempts to prepare corresponding compounds with other alkali hypophosphites yielded salts of the series $R[(UO_2)_2(H_2PO_2)_5]$. The compounds form uranyl hypophosphite, and ten or more molecular proportions of alkali hypophosphite could not be caused to crystallize.

H. Rose obtained **manganese hypophosphite**, $Mn(H_2PO_2)_2.H_2O$, by boiling the calcium salt with manganese oxalate; and C. A. Wurtz, and C. F. Rammelsberg, by the double decomposition of barium hypophosphite and manganese sulphate. The small, rose-red crystals are believed by C. F. Rammelsberg to be monoclinic prisms. They lose no water at 100°, but become anhydrous at 150°, according to C. A. Wurtz, and at 180°–200°, according to C. F. Rammelsberg, and when heated to a higher temp. phosphine is evolved and some red phosphorus is formed: $5Mn(H_2PO_2)_2=2Mn_2P_2O_7+Mn(PO_3)_2+4PH_3+4H_2$. H. Rose prepared **ferrous hypophosphite**, $Fe(H_2PO_2)_2.6H_2O$, in small green crystals—said to be octahedral, but see the magnesium salt—by dissolving iron in hypophosphorous acid out of contact with air; and C. A. Wurtz, by the double decomposition of the barium salt with ferrous sulphate. The aq. soln. on evaporation furnishes crystals of the salt. It is readily oxidized by exposure to air. H. Rose said that hydrated ferric oxide can be dissolved in the cold acid without reduction, forming a white **ferric hypophosphite** which is sparingly soluble in the free acid, and yields spontaneously inflammable phosphine when heated. When hydrated ferric oxide is boiled with hypophosphorous acid, a soln. of ferrous hypophosphite is obtained, and ferric phosphate is precipitated. The stability of ferric hypophosphite is remarkable in that tervalent iron is associated with a strongly reducing acid. W. Hieber represented the constitution of the normal salt, $Fe(H_2PO_2)_3$ by $[Fe_3(H_2PO_2)_6](H_2PO_2)_6$, where $[Fe_3(H_2PO_2)_6]$ is considered to be a basic, tervalent radicle. He obtained this salt by slowly adding a hot soln. of ferric chloride to a hot soln. of sodium hypophosphite, so that the precipitate first formed is dissolved. It can also be made by treating ferric hydroxide freshly precipitated in the cold, with hypophosphorous acid. The normal salt is also obtained by digesting the basic ferric hypophosphites with the acid. By working with less conc. soln., a series of **ferric hydroxyhypophosphites** was prepared. Thus, *triferric hydroxyhexaphosphitodihypophosphite*, $[Fe_3(OH)(H_2PO_2)_6](H_2PO_2)_2+24H_2O$, was obtained; likewise the complex $[Fe_3(OH)(H_2PO_2)_6](H_2PO_2)[Fe_3(H_2PO_2)_6(OH)_2]H_2PO_2+nH_2O$; as well as *triferric dihydroxyhexahypophosphitohypophosphite*, $[Fe_3(H_2PO_2)_6(OH)_2]H_2PO_2+nH_2O$; and *triferric trihydroxypentahypophosphitohypophosphite*, $[Fe_3(H_2PO_2)_5(OH)_3]H_2PO_2+nH_2O$. If triferric hydroxyhexahypophosphitodihypophosphite be warmed with a soln. of potassium hypophosphite, there is formed **potassium aquopentahypophosphitoferrate**, $K_2[Fe(H_2O)(H_2PO_2)_5]$, and similarly for **sodium aquopentahypophosphitoferrate**, $Na[Fe(H_2O)(H_2PO_2)_5]$. Another series of complex ferric hydroxy- or aquohypophosphites has been prepared:

$[Fe_3(HO)(H_2PO_2)_6](H_2PO_2)_2.nH_2O$;
$[Fe_3(HO)(H_2PO_2)_6]_2[Fe(H_2O)(H_2PO_2)_5](H_2PO_2)_2$;
$[Fe_3(H_2PO_2)_6][Fe(H_2O)(H_2PO_2)_5][Fe_3(HO)(H_2PO_2)_6](H_2PO_2)_3$;
$[Fe_3(HO)(H_2PO_2)_6][Fe(H_2O)(H_2PO_2)_5$;
$[Fe_3(H_2PO_2)_6][Fe(H_2O)(H_2PO_2)_5$;
$[Fe_3(H_2PO_2)_6][F_3(HO)(H_2PO_2)_6[Fe(HO)(H_2PO_2)_5(H_2PO_2)_2$;
$[Fe_3(H_2PO_2)_6]_2[Fe(HO)(H_2PO_2)_5](H_2PO_2)_3$;
$[Fe_3(H_2PO_2)_6][Fe(H_2O)(H_2PO_2)_5](H_2PO_2)$.

W. Hieber prepared a number of complex **ferric sulphatohypophosphites,** $[Fe_3(H_2PO_2)_6]SO_4(H_2PO_2).4H_2O$; $[Fe_3(H_2PO_2)_6]\frac{1}{2}SO_4(H_2PO_2)_2.4H_2O$; $[Fe_3(H_2PO_2)_6](HSO_4)_3.nH_2O$; $[Fe_3(H_2PO_2)_6]_2(HSO_4)_2(H_2PO_2)_2SO_4.24H_2O$; $[Fe_3(H_2PO_2)_6]_2\frac{1}{2}SO_4(HSO_4)_4(H_2PO_2).30H_2O$; $[Fe_3(H_2PO_2)_6][Fe_3(H_2PO_2)_6(OH)](SO_4)_2(H_2PO_2).24H_2O$; $[Fe_3(H_2PO_2)_6(OH)].nH_2O$. The **ferric perchloratohypophosphites :** $[Fe_3(H_2PO_2)_6](ClO_4)_2H_2PO_2.\frac{1}{2}H_3PO_2.18H_2O$; and $[Fe_3(H_2PO_2)_6](ClO_4)(H_2PO_2)_2.nH_2O$. The **ferric chlorostibnohypophosphite :** $[Fe_3(H_2PO_2)_6]_2(SbCl_6)_3(H_2PO_2)_3.18H_2O$. The **ferric chlorohypophosphites :** $[Fe_3(H_2PO_2)_6][FeCl_4](H_2PO_2)_2.2H_3PO_2.10H_2O$; $[Fe_3(H_2PO_2)_6][FeCl_3(H_2PO_2)]_2H_2PO_2.12H_2O$; $[Fe_3(H_2PO_2)_6][FeCl_3.(H_2PO_2)][FeCl_4)H_2PO_2.6H_2O$; and $[Fe_3(HO)(H_2PO_2)_6]_2Cl_2(H_2PO_2).15H_2O$. The **ferric bromohypophosphite :** $[Fe_3(H_2PO_2)_6][FeBr_4](H_2PO_2)_2.12H_2O$. The **ferric nitratohypophosphite :** $[Fe_3(H_2PO_2)_6][Fe_3(HO)(H_2PO_2)_6](H_2PO_2)_3(NO_3)_2).24H_2O$.

H. Rose dissolved freshly precipitated cobalt hydroxide in cold hypophosphorous acid, and evaporated the filtered soln. in vacuo, whereby red crystals of **cobalt hypophosphite,** $Co(H_2PO_2)_2.6H_2O$, isomorphous with the magnesium salt are formed. S. Stevanovic, and J. Beckenkamp showed that the crystals are tetragonal bipyramids with the axial ratio, according to the former, $a : c = 1 : 0{\cdot}9892$. Twinning occurred about the (101)-face ; the corrosion figures were found to be approximately equiangular and three-sided. The birefringence is feeble and positive. F. W. Clarke gave 1·808–1·811 for the sp. gr. of the salt at 18·5°. C. A. Wurtz found that the water of crystallization is lost at 100° ; and C. F. Rammelsberg, at 120°–130° ; the salt begins to decompose at 150° ; and it becomes black : $3Co(H_2PO_2)_2 = 2Co(PO_3)_2 + CoP + PH_3 + 9H$. When evaporated with nitric acid, H. Rose found that the hypophosphite is converted into the metaphosphate. H. Rose, and C. A. Wurtz prepared **nickel hypophosphite,** $Ni(H_2PO_2)_2.6H_2O$, by the methods employed for the cobalt salt. The green crystals, said H. Rose, appear to be cubes ; and C. A. Wurtz, and C. F. Rammelsberg, octahedra isomorphous with the cobalt salt. F. W. Clarke gave 1·856 for the sp. gr. of the salt at 18° ; 1·844 at 19° ; and 1·824 at 19·8°. C. A. Wurtz found the salt is dehydrated at 100° ; and C. F. Rammelsberg said the decomposition begins at 100°, and he represented the reaction by $3Ni(H_2PO_2)_2 = 2Ni(PO_3)_2 + NiP + PH_3 + 9H$. The salt is soluble in water ; and when the soln. is evaporated at 100°, some nickel is reduced. The moist crystals are also reduced if heated quickly to 120°. The stability of the *nickel amminohypophosphite* was discussed by F. Ephraim and co-workers.

R. Engel prepared **platinous hypophosphite,** $Pt(H_2PO_2)_2$, by passing phosphine at 0° into a soln. of platinic chloride in 90 per cent. alcohol acidified with a drop of hydrochloric acid ; it is washed with alcohol and then with boiling water ; dried in the cold, and then at 130°. The yellow salt is not altered at 130°, but it decomposes at a higher temp. into spontaneously inflammable phosphine. It is insoluble in water, alcohol, and in hydrochloric, sulphuric, and acetic acids ; it is soluble with oxidation in nitric acid, and chlorine-water. Boiling conc. potash-lye decomposes it with the evolution of hydrogen and the deposition of platinum. Placed in suspension in soln. of gold, silver, copper, mercury, or palladium, it immediately reduces these salts in the cold, and is itself partially reduced.

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§ 16. Phosphorus Trioxide, or Phosphorous Oxide

In 1777, B. G. le Sage[1] passed a very slow current of well-dried air through a tube containing fragments of phosphorus at a low temp., and obtained a white, flocculent powder of what must have been *phosphorous anhydride*, **phosphorous oxide**, or **phosphorus trioxide**, P_2O_3, or rather P_4O_6. This substance was at first confused with *les fleurs de phosphore* obtained by the combustion of phosphorus in air. A. L. Lavoisier recognized the difference dependent on the conditions under which the phosphorus is burnt, and he inferred the existence of two oxides of phosphorus—one, made by B. G. le Sage, *spontanément à l'air par la destruction lente du phosphore*, and the other obtained *par combustion*. P. A. Steinacher,[2] and H. Davy, also recognized that phosphorous oxide and some phosphoric oxide are produced by the slow oxidation of phosphorus; but the relationship between the two oxides was not made clear until P. L. Dulong's memoir: *Sur les combinaisons du phosphore avec oxygène* in 1816, when it was shown that the two oxides are related to phosphorus much as the two oxides of carbon are related to carbon. The slow oxidation of phosphorus has been previously discussed—*vide supra.*

Phosphorous oxide is produced by the imperfect combustion of phosphorus, such as occurs when that element is warmed in contact with a limited supply of air, slowly renewed, or much rarefied. P. A. Steinacher heated phosphorus to 100° in a narrow glass tube containing air, and found that phosphorous oxide, accompanied by a small proportion of phosphoric oxide, sublimes. J. J. Berzelius burnt the phosphorus in a glass tube through which only a very slow current of air was passed; and H. Davy heated the phosphorus in highly rarefied air. J. M. Cabell sublimed the product at about 177° in an atm. of hydrogen. According to E. Jungfleisch, the oxidation of pure dry phosphorus at low temp. in pure oxygen at atm. press. gives exclusively phosphoric oxide, but at press. of 18–20 mm. the immediate products of oxidation are phosphorous oxide and a bright yellow oxide—the tetritoxide. When oxidized in oxygen at low press., the phosphorus becomes very luminous, partially fuses, and soon ignites with a large pale glaucous flame which is extinguished in a few moments, all the oxygen being absorbed. After cooling, the unchanged phosphorus is left surrounded by phosphoric oxide (formed before the reduction in press.), by the yellow compound (a little farther away), and lastly by a white aureole of phosphorous oxide. On admission of a very small quantity of air, the vapour of the latter burns with a phosphorescent glow, whilst a larger quantity of air causes the ignition first of the solid P_2O_3, and then of the remaining phosphorus. Introduction of water instead of air into the combustion vessel produces bright flashes of light, as the dissolved oxygen oxidizes small quantities of P_2O_3 vapour. The resulting soln. contains phosphoric and phosphorous acids with the yellow compound in suspension, the phosphorous acid amounting to 57·9 per cent. of the total phosphorus. The oxidation in this manner can be effected continuously in a tube, and the P_2O_3 obtained in well-defined crystals. Whether air, pure oxygen, or oxygen mixed with an inert gas is used at low press. the products of oxidation are the same. Partial oxidation of phosphorus in this manner renders it spontaneously inflammable, owing to the inflammability of the phosphorous oxide formed. According to R. Cowper and V. B. Lewes, when dry air is passed over molten phosphorus, the product contains 70·1 to 78·2 per cent. of phosphoric oxide, 3·2 to 9·6 per cent. of phosphorous oxide, and 17·0 to 26·6 per cent. of yellow phosphorus which changes into red phosphorus on exposure to light as noted by A. Irving, who overlooked the presence of yellow phosphorus. A. Sommer described some methods of burning phosphorus in a limited supply of air. T. E. Thorpe and A. E. H. Tutton employed the following mode of preparing phosphorous oxide by this process:

The phosphorus is placed in a glass tube, *A*, which is bent as shown in Fig. 31, and fitted into one end of a long tube cooled by a jacket, *B*, containing water at 60°. The cooled tube is fitted to a U-tube, *C*, immersed in a freezing-mixture; a plug of glass-wool is placed in the condenser tube near the U-tube. The phosphorus is ignited, and a slow stream of air is drawn through the apparatus by means of an aspirator connected to the U-tube. The phosphorus pentoxide is arrested by the glass-wool, and phosphorus oxide passes into the U-tube, where it is condensed into a white crystalline mass. The wash-bottle, *E*, with conc. sulphuric acid protects the product from moisture. At the end of the experiment, the solid in the U-tube can be melted and run into the bottle *D*.

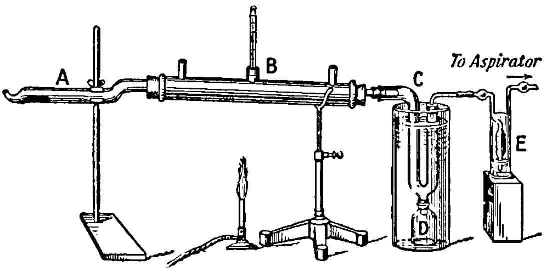
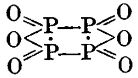


FIG. 31.—The Preparation of Phosphorus Trioxide.

A. Naquet said that phosphorous oxide is formed by the action of phosphorus trichloride on phosphorous acid: $H_3PO_3+PCl_3=3HCl+P_2O_3$. The reaction was studied by A. Gautier, A. Besson, and K. Kraut. A. Béchamp obtained this oxide by the action of phosphorus trichloride on acetic anhydride: $3(CH_3CO)_2O+2PCl_3=6CH_3COCl+P_2O_3$; and T. E. Thorpe, and C. H. Bothamley and G. R. Thompson found that the reaction with acetic acid is analogous: $3CH_3COOH+2PCl_3=3CH_3COCl+3HCl+P_2O_3$—propionic and butyric acids give similar results. There are a number of side reactions, and some phosphorus tetritoxide is formed (*q.v.*).

P. A. Steinacher reported that phosphorous oxide forms white bulky flakes which smell like garlic; the oxide possesses a sour sharp taste; and reddens moist litmus, but not that which is dry. J. M. Cabell showed that the sublimed oxide consists of monoclinic **crystals.** T. E. Thorpe and A. E. H. Tutton reported that the sublimed oxide in the cooler part of the condensing tube consists of minute crystals aggregated into a snow-white mass; in the warmer parts, radiating aggregates of crystals are formed; and when the melted oxide is cooled, or when the soln. of the oxide in benzene or carbon is evaporated, well-defined crystals are obtained. Exact measurements of the crystals are not possible because of the oxidation and deliquescence of the oxide on exposure. The crystals are in all cases monoclinic, and there is no evidence of dimorphism such as occurs with arsenious and antimonious oxides. The crystals show the pinacoidal faces, *a*(100) and *b*(010), several prism faces, a pair of complementary pyramidal forms. The extinctions upon *a* are parallel to the prism edges, whilst those on *b* make an angle of about 20° with the prism edges. In convergent light an optic axis with its system of rings is seen on looking through the orthopinacoid *a* towards the edge of the field in the direction indicated in one of the crystals shown in Fig. 4. When the crossed Nicols are parallel to the axial edges, the brush passes across the centre of the field in a line parallel to the vertical axis. The optic axial plane, therefore, appears to be the symmetry plane *b*. As phosphorous oxide is also in all probability monoclinic, with an extinction upon the symmetry plane of about 20°, it would appear that there is a regular relationship between phosphorous, arsenious, and antimonious oxides, such that there is a gradual approach to the higher symmetry of the rhombic system which is ultimately attained by antimonious oxide. The optic axial plane is also identical with the symmetry plane in phosphorous and arsenious oxides, and also for all the colours of the spectrum, with the exception of red, for which colour the plane crosses to one at right angles, as in the case of antimonious oxide.

The **vapour density** found by T. E. Thorpe and A. E. H. Tutton is 7·67 to 7·83 at temp. ranging from 131° to 184°. The theoretical value for P_2O_3 is 3·81, and that for P_4O_6 is 7·62. Hence, the formula P_4O_6. This is in agreement with the effect of this oxide on the f.p. of benzene; and, according to R. Schenck and co-workers, on the f.p. of naphthalene. G. le Bas' observations on the mol. vol. are in agreement with the formula:



T. E. Thorpe and A. E. H. Tutton found the **specific gravity** of the liquid oxide to be 1·9431 at 21°/4°, and there is a 9·0 per cent. contraction on solidification so that the sp. gr. of the solid oxide is 2·135 at 21°/4°. The sp. gr. of the oxide at its b.p., 173·1°, is 1·6897, and the **specific volume,** 130·2. Accepting H. Kopp's and H. Buff's value 7·8 for the sp. vol. of oxygen joining to different atoms by single linkages, the sp. vol. of free phosphorus is 20·9, and the calculated sp. vol. of phosphorus in combination as phosphorous oxide has the same value. This is taken to mean that the phosphorus in both cases is quinquevalent. According to T. E. Thorpe and A. E. H. Tutton, the relative vol., *v*, of the molten oxide is:

	27·10°	36·07°	63·20°	89·48°	117·68°	140·30°
Vol. . . .	1·0000	1·0078	1·0316	1·0557	1·0827	1·1058

these results, corrected for the thermal expansion of glass, can be represented by $v=1+0{\cdot}0_3 91377\theta-0{\cdot}0_6 11175\theta^2+0{\cdot}0_8 38607\theta^3$, when θ° ranges betwccn 27·10° and 140·30°. The **thermal expansion** of the liquid follows directly from:

	25°	30°	50°	75°	100°	125°	150°	170°	173 1°
Vol. . .	1·000	1·0046	1·0228	1·0459	1·0695	1·0941	1·1200	1·1419	1·1454

Phosphorous oxide has the **melting point** 22·5°, when it forms a clear, colourless liquid which freezes at 21°, and has a marked tendency to undercooling. R. Schenck and co-workers gave for the **vapour pressure,** p mm. of the liquid:

	22·4°	30·8°	40·8°	50·0°	64·4°	72·7°	91·2°
p . .	2·7	4·1	6·0	9·5	18·4	50·8	297·9

T. E. Thorpe and A. E. H. Tutton showed that the **boiling point** is 173·1° at 760 mm. There is no decomposition at this temp. in an atm. of an inert gas—nitrogen, or carbon dioxide. Phosphorous oxide is a comparatively stable substance up to temp. of about 200°. When heated in a sealed tube, the clear liquid becomes turbid at about 210°, and at a somewhat higher temp. the solid substance which separates out gradually becomes yellow, and ultimately dark red. At 300°, a considerable quantity of the red solid is formed, but there is still a large proportion of the liquid undecomposed, even after an hour's heating at this temp. At the temp. of boiling sulphur, 440°, the whole of the oxide is decomposed into solid products—red phosphorus and phosphorus tetroxide: $2P_4O_6=3P_2O_4+2P$. J. Ogier estimated for the **heat of formation,** $\frac{1}{2}(P_2O_3)=122{\cdot}1$ Cals.; and M. Berthelot, $(P,\frac{1}{2}O_3)=\frac{1}{2}P_2O_3+37{\cdot}4$ Cals. These values are quite unreliable.

A. Strecker, and A. Irving showed that white phosphorous oxide, prepared by the slow burning of phosphorus, quickly turns yellow, and ultimately red on exposure to sunlight. It is assumed that the phosphorous oxide is itself decomposed: $5P_2O_3=4P+3P_2O_5$. R. Cowper and V. B. Lewes attributed (i) the colour change; and (ii) the spontaneous inflammation which occurs when the oxide is thrown into the air, to the presence of finely-divided phosphorus associated as an impurity with the phosphorous oxide—*vide supra.* T. E. Thorpe and A. E. H. Tutton showed that phosphorous oxide obtained by their mode of preparation slowly becomes yellow in diffused daylight and rapidly in sunlight. About 0·8 to 1·0 per cent. of red phosphorus may be produced in 4 to 6 months' exposure. Fig. 32 shows the intensity of the colour change which occurred when a tube was placed in the solar spectrum for 3 hrs. The dotted curve is supposed to represent the sensitiveness of the oxide to change in diffcrent parts of the spectrum. The maximum change occurs between the F- and the G-lines. If the reddened oxide be melted, filtered, and distilled, it is again reddened by light, but if these operations be repeated four times, the product remained clear and colourless after 12 months' exposure. The insensitive oxide has not been obtained by distillation at ordinary temp. in vacuo, but isolated crystals may be found which have not reddened in light. The **index of refraction,** μ, for light of wave-length λ, at 27·4°, is:

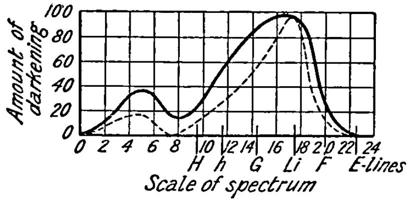
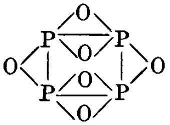


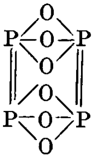
Fig. 32.—The Effect of Different Parts of the Spectrum on the Colour Change of Phosphorous Oxide.

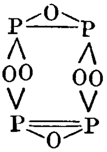
	Li-line.	C-line.	D-line.	Tl-line.	F-line.	G-line.
λ .	6705	6562	5892	5348	4861	4340
μ .	1·5350	1·5358	1·5403	1·5454	1·5518	1·5616

The results at 27·4° were represented by $\mu=1{\cdot}5171+817670\lambda^{-2}-316590000000\lambda^{-4}$. The **refraction equivalent** for the A-line is 60·5, and for the ray of infinite wave-length, 58·9. F. Zecchini calculated 21·4 for the mol. refraction with the μ-formula, and 14·25 with the μ^2-formula. H. J. Emeléus found the spectrum of glowing phosphorous oxide is the same as that of burning and of glowing phosphorus—*vide supra*, the oxidation of phosphorus. T. E. Thorpe and A. E. H. Tutton found the **dispersion** for the *H*- and *A*-lines to be 0·0366, and the **dispersion equivalent,** 4·17. O. Stelling studied the X-ray spectrum. The sp. **magnetic rotation** at 24·75° is 1·5832, and the mol. magnetic rotation 9·962. This agrees with the general rule that free phosphorus has a larger value than when combined with oxygen. R. Schenck and co-workers found the sp. **electrical conductivity** of phosphorous oxide at 25° to be $1{\cdot}2\times10^{-7}$, and the **dielectric constant,** 3·2 at 22°.

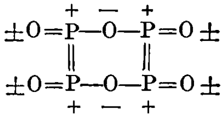
Analyses by J. J. Berzelius, H. Davy, T. Thomson, P. L. Dulong, and T. E. Thorpe and A. E. H. Tutton are in agreement with the empirical formula P_2O_3; and the vapour density and cryoscopic observations with P_4O_6. The observations on the sp. vol. indicate that the oxygen atoms are joined to the phosphorus atom by single linkages, and that the phosphorus atom is quinquevalent. This gives as possible formulæ:







H. Henstock gave for the electronic structure:



$$\begin{array}{ccccccccc} & & + & & - & & + & & \\ \pm O & = & P & - & O & - & P & = & O\pm \\ & & \| & & & & \| & & \\ \pm O & = & P & - & O & - & P & = & O\pm \\ & & + & & - & & + & & \end{array}$$

Since it has been shown that the vapour of phosphorus in air is mainly phosphorous oxide, the physiological action of phosphorus vapour is really that of the vapour of phosphorous oxide. F. Wöhler and F. T. Frerichs, P. Schulz, J. Personne, B. von Dybkowsky, etc., have discussed the toxic action of phosphorous oxide. According to T. E. Thorpe and A. E. H. Tutton, **hydrogen** has no action on hot or cold phosphorous oxide; but when exposed to **air** or **oxygen,** spontaneous oxidation to phosphorus pentoxide occurs. When a few decigrams of phosphorous oxide are placed at the bottom of a wide tube closed at one end, and previously filled with dry oxygen, and the tube sealed and kept in the dark, in an upright position, a bulky, snow-like deposit of pure phosphoric oxide is formed in rhythmic striæ or annuli along the walls of the tube, showing that vaporization of the phosphorous oxide precedes its oxidation. The action is comparatively slow at first, but seems to proceed at an accelerated rate as the press. of the included oxygen diminishes, whereby the volatility of the phosphorous oxide is increased. Under diminished press. the tube becomes more or less filled with a luminous fluctuating glow, which instantly stops when the press. is increased to that of the atm. By increase of temp., effected by warming the outside of the tube with a water-jacket, the diminution of press. required to produce the glow becomes less—a further proof that the glow is due to the action of oxygen on the *vapour* of phosphorous oxide. If the temperature is gradually raised to about 70°, the rate of volatilization, and consequent oxidation, is such that the mass of phosphorous oxide burns, but the vigorous combustion can be at once stopped by reducing the press. of the oxygen, and immediately renewed by restoring the press., and the experiment can be repeated until the whole of the oxide or the oxygen is used up. The change from glow to actual flame is perfectly regular and gradual, and is unattended with any sudden increase in brilliancy. No ozone is formed as the oxidation proceeds. This fact supports the assumption that the formation of ozone during the glow of phosphorus is caused by the dissociation of the oxygen mol. in the formation of phosphoric oxide: $P_2+3O_2=P_2O_5+O$, and $O+O_2=O_3$. When phosphorous oxide is converted into the pentoxide, no dissociation of oxygen mols. need be assumed to occur: $P_4O_6+2O_2=2P_2O_5$. These phenomena are so very similar to those which occur with phosphorus alone that it might be thought that the glow observed in the case of phosphorous oxide is due to the presence of free phosphorus in that compound. The amount of free phosphorus required to produce a glow is so very small that the supposition cannot be at once dismissed as impossible. The absence of the ozone and the gradual increase in the intensity of the glow, until it passes into steady combustion as the temp. is increased, seem convincing that phosphorous oxide phosphoresces in contact with oxygen like phosphorus itself, and under very similar conditions. Moreover, no hydrogen dioxide could be detected when the glow occurred in moist air, whereas the glow of phosphorus under the same conditions is attended with the production of notable quantities of that substance. E. Jungfleisch, R. Schenck and co-workers, E. Scharff, L. and E. Bloch, H. B. Weiser and A. Garrison, and E. Gilchrist attributed the luminescence of phosphorus entirely to the oxidation of phosphorus trioxide. W. E. Downey showed that light from oxidizing phosphorus trioxide, like that from phosphorus, is capable of ionizing oxygen; and H. J. Emeléus, that the spectra of glowing phosphorus, phosphorus trioxide, and burning phosphine are the same. H. Rinde inferred that in dry oxygen, phosphorus trioxide is oxidized directly to the pentoxide without glow, but in moist oxygen, an intermediate compound, possibly phosphine, is formed. C. C. Miller also showed that water-vapour is necessary for the glow; and that phosphine is always formed, and liquid phosphorus hydride as well. The production of this liquid accounts for the rise of press. to a maximum when phosphorus trioxide is in the presence of water-vapour at 2·5 to 5·0 mm. press. The subsequent fall of press. is attributed to the interaction of phosphorus hydride and trioxide. At 25°, in oxygen at 600 mm., and in the presence of water-vapour, the phosphorus oxidizes directly to the tetroxide, not the pentoxide. W. E. Downey showed that ozone is formed during the oxidation of the trioxide; this is taken to mean that oxygen is oxidized by the light of the glow which has the wave-length $\lambda=1200$ A. to 1800 A.

Melted phosphorous oxide readily takes fire in the air, especially when gently warmed or when spread out over the surface of paper or cloth. Thrown into oxygen heated to 50° or 60°, it instantly ignites with a flame of almost blinding brilliancy. Great care is necessary to exclude air from the apparatus during the process of distillation of phosphorous oxide. If air is permitted to enter the distilling vessel, the vapour of the oxide at once ignites, and may set fire to the liquid, with the possibility of a dangerous explosion. According to R. Schenck and co-workers, dry oxygen has scarcely any action on phosphorous oxide at 10°; 40° is the most favourable temp. for measuring the speed of oxidation which is then proportional to the square root of the press. of the oxygen. This is taken to mean that the reaction is semi-molecular, and is effected by atoms—*vide supra*, oxidation of phosphorus. When air charged with **ozone** is passed over a small quantity of phosphorous oxide, the oxide glows continuously, without the pulsating appearance which characterizes its glow in air or in oxygen under diminished press. The glow ceases when the silent discharge is interrupted, but recommences immediately it is resumed. The glow in the case of the ozonized oxygen, at atm. press., is close to the oxide, and not, as in the case of air, or in rarefied oxygen, at some distance away from it. Moreover, after a time, owing apparently to the energy of the reaction, the phosphorous oxide melts, whereas it never melts in pure oxygen or in air at the ordinary temp.

Phosphorous oxide was formerly stated to deliquesce rapidly in air, and to dissolve in **water** with a hissing noise; indeed, J. J. Berzelius said that the attraction of the anhydride for the moisture of the air develops so much heat that the oxide takes fire. The ignition of phosphorous oxide when shaken in air was shown by R. Cowper and V. B. Lewes to be due to the presence of very finely-divided yellow phosphorus —*vide supra*—and the hissing noise developed by contact with water is probably due to the presence of phosphorus pentoxide, because T. E. Thorpe and A. E. H. Tutton found that phosphorous oxide is somewhat inert in its attraction for water. Both the solid and the liquid form dissolve only with great slowness; a few grams will remain for several days in contact with water without any considerable diminution in bulk being apparent. On long standing, the pure oxide completely dissolves; the soln. has a strong acid reaction and an alliaceous smell; and its general properties show that phosphorous oxide is slowly converted into phosphorous acid by the action of cold water. When a small quantity of water, not lower than 15° in temp., is added to a quantity of phosphorous oxide, not less than one-sixth its bulk, the slight rise of temp., probably due to the formation of phosphorous acid at the surface of contact, is just sufficient after about 10 minutes to melt the oxide which remains unmixed with the water at the bottom of the vessel. This slowly dissolves, as above described, and in a few days forms a soln. of phosphorous acid. When the water is heated, the reaction is entirely different. At temp. below 100°, it is very energetic; large quantities of red phosphorus or the red suboxide are formed with an explosive evolution of spontaneously inflammable phosphoretted hydrogen and the formation of phosphoric acid. With quantities of phosphorous oxide exceeding a couple of grams, hot water produces most violent explosions. A cold dil. soln. of **alkali hydroxide** resembles cold water in its action on phosphorous oxide. No action is apparent at first, but, on standing, the oxide is dissolved, and a phosphite is formed. Cold conc. or hot dil. soln. decompose the oxide with production of red phosphorus, or the tetritoxide, and a phosphate, whilst spontaneously inflammable phosphine is evolved. When phosphorous oxide is thrown into a jar of **chlorine,** it instantly ignites, and burns with a greenish flame. In a slow current of dry chlorine, the oxide becomes very hot, and burns with a pale green flame scarcely perceptible in daylight. If the flask containing the phosphorous oxide is surrounded by ice, and the current of chlorine is not too rapid, the whole of the oxide is gradually converted into a clear liquid which does not solidify in cold water. On distilling this liquid, the thermometer rises rapidly to 107°, and remains constant at this temp. for some time, after which it suddenly rises to 200°, and the residue in the flask becomes viscid. The condensate is phosphoryl chloride, and the viscid residue is metaphosphoryl chloride, PO_2Cl, and the reaction is therefore symbolized: $P_4O_6+4Cl_2=2POCl_3+2PO_2Cl$. Phosphorous oxide reacts violently with liquid **bromine,** and the mass generally inflames. When the oxide at ordinary temp. is continuously acted on by bromine vapour, lemon-yellow crystals of phosphorus pentabromide are formed above the oxide, while the oxide itself becomes covered with a white amorphous powder of phosphorus pentoxide: $5P_4O_6+20Br_2=8PBr_5+6P_2O_5$. The crystals of the pentoxide afterwards dissolve in the excess of bromine which condenses on them, the pentabromide is washed down, and a second reaction occurs resulting in the formation of phosphoryl bromide, and metaphosphoryl bromide: $P_4O_6+4Br_2=2POBr_3+2PO_2Br$, as in the case of chlorine. Phosphorous oxide reacts slowly with **iodine,** forming an orange-red solid. Even when the substances are heated together in a sealed tube at 150°, the reaction is far from complete. When the two substances are heated, under press., with a quantity of carbon bisulphide, phosphoric oxide is formed, and orange-red prisms of P_2I_4 separate out from the conc. soln. No formation of the tri-iodide could be detected. The main reaction is probably in accordance with the equation $5P_4O_6+8I_2=4P_2I_4+6P_2O_5$. Phosphorous oxide rapidly absorbs **hydrogen chloride,** forming a viscous mass and a clear, mobile liquid. The semi-solid substance is at first quite white, but as the reaction proceeds it changes to yellow and orange. The clear liquid consists of phosphorus trichloride, boiling at 76°; the semi-solid residue is, for the most part, soluble in water, and the soln. contains phosphorous and phosphoric acids. The yellow solid was free phosphorus. The main reaction is symbolized: $P_4O_6+6HCl=2PCl_3+2H_3PO_3$; and the phosphorous acid reacts with the trichloride as symbolized by A. Geuther: $PCl_3+4H_3PO_3=3H_3PO_4+2P+3HCl$.

When phosphorous oxide and **sulphur** are heated together in an atm. of nitrogen or carbon dioxide, the two substances melt, and form separate layers of liquid; at about 160° a violent reaction occurs, no gas is produced, but the liquid becomes solid owing to the direct addition of sulphur, forming phosphorus disulphotrioxide, analogous to phosphorus pentoxide: $P_4O_6+4S=P_4O_6S_4$. The reaction with **selenium** appears to be similar to that with sulphur, but the phosphorous oxide itself is largely decomposed at the temp. of the reaction. Phosphorous oxide does not react with **sulphur dioxide**, hot or cold. The vapour of **sulphur trioxide** reacts with phosphorous oxide at ordinary temp., forming sulphur dioxide and white flocks of phosphorus pentoxide; no compound was detected other than the products of the oxidation of phosphorous oxide at the expense of the sulphur trioxide. When conc. **sulphuric acid** is dropped on phosphorous oxide there is a great rise of temp., and sulphur dioxide is liberated and the phosphorous oxide becomes oxidized to phosphoric acid. When quantities of a gram and upwards are employed, the reaction is so violent that the mass generally ingnites. **Sulphur chloride**, S_2Cl_2, acts with great violence on phosphorous oxide, forming phosphoryl and thiophosphoryl chlorides, free sulphur, and sulphur dioxide: $P_4O_6+6S_2Cl_2=2POCl_3+2PSCl_3+2SO_2+8S$. H. Prinz said that no reaction occurs even at 230°.

According to T. E. Thorpe and A. E. H. Tutton, **nitrogen** has no action on hot or cold phosphorous oxide; but **ammonia** slowly reacts in the cold, absorbing between 7 and 8 mols. of gas per mol. of oxide. When ammonia is led over phosphorous oxide melted by the warmth of the hand, in an apparatus previously filled with nitrogen, a somewhat violent reaction occurs with production of a white cloud; the mass ignites, and a considerable quantity of amorphous phosphorus or the red suboxide is formed. The violence of the reaction may, however, be controlled by surrounding the flask with iced water. The reaction is more easily regulated if the phosphorous oxide be dissolved in ether or benzene. There is formed phosphorous diamide, $HO.P(NH_2)_2$ (*q.v.*). The **substituted ammonias** react similarly. Phosphorous oxide does not react with **nitric oxide**—hot or cold, but with **nitrogen peroxide** it forms phosphorus pentoxide and the lower oxides of nitrogen. No compound of nitrogen peroxide and phosphorous oxide is formed. Phosphorous oxide does not react with **phosphine**—hot or cold. At ordinary temp., **phosphorus trichloride** and phosphorous oxide are miscible without reaction, and they can be separated by distillation; if the mixture be heated in a sealed tube at 180° for some hours, there is formed, not phosphoryl chloride, but a mixture of red phosphorus and phosphorus pentoxide and pentachloride. The reaction between **phosphorus pentachloride** and trioxide is violent at ordinary temp., forming a product which is liquid when the vessel is cooled by ice: $P_4O_6+6PCl_3=6POCl_3+4P$. According to L. Amat, phosphorous oxide and **phosphorous acid** react when heated forming solid hydrogen diphosphide. F. Krafft and R. Neumann found that when **arsenic** is heated with phosphorous oxide for 6 hrs. in an atm. of carbon dioxide in a sealed tube at 290°, the arsenic quantitatively displaces the phosphorus: $4As+P_4O_6=4P+As_4O_6$; **antimony** acts similarly.

Cold or warm phosphorous oxide was found by T. E. Thorpe and A. E. H. Tutton to have no action on **ethylene, carbon monoxide, carbon dioxide,** or **cyanogen.** The oxide dissolves without reaction in **carbon disulphide, benzene, chloroform,** and **ether.** Although phosphorous oxide reacts very slowly with water at ordinary temp., it ignites when brought in contact with **ethyl alcohol**; and by allowing the reaction to proceed gradually in a well-cooled vessel, diethyl phosphite is formed: $P_4O_6+8C_2H_5OH=2H_2O+4(HO)P(OC_2H_5)_2$, a reaction studied by T. E. Thorpe and B. North.

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§ 17. Phosphorous Acid

As indicated in connection with phosphorous oxide, **phosphorous acid,** H_3PO_3, must have been known for a long time as a product of the slow oxidation of phosphorus in moist air. In 1777, B. G. le Sage[1] described the character of an acid which he obtained from the products of the slow combustion of phosphorus, and which had properties somewhat different from A. L. Lavoisier's phosphoric acid. This acid liquid was at first confused with phosphoric acid, since it was assumed that different acids were obtained by the slow and rapid combustion of phosphorus; the one was at first called *acidum phosphori per deflagrationem,* and the other *acidum phosphori per deliquium.* These two acids were later distinguished as *acide phosphorique* and *acide phosphoreux.* B. G. le Sage obtained the liquid by exposing sticks of phosphorus to moist air and collecting the liquid which was formed. The stick of phosphorus was very liable to inflame owing to the too rapid oxidation; to avoid this B. Pelletier enclosed each stick of phosphorus in a glass tube. In B. Pelletier's process for making phosphorous acid by the slow oxidation of phosphorus, each pencil of phosphorus was contained in a glass tube drawn out at one end to a fine orifice. These glass tubes, to the number of 30 or 40, were placed in a funnel the beak of which was passed into a bottle standing in a plate of water, and the whole was covered with a bell-glass with inlet and outlet for a small current of air. The phosphorus slowly oxidized, and the product deliquesced and dripped into the bottle. C. F. Bucholz placed the sticks of phosphorus in the upper part of an inclined shallow dish kept at a temp. not exceeding 10°. The acid accumulates in the lower part of the dish, and amounted to over five times the weight of the phosphorus employed. Various ways of conducting this experiment have been discussed by A. Sommer, H. A. von Vogel, T. Salzer, P. Drawe, C. Bansa, and A. Rosenheim and co-workers—*vide infra,* hypophosphoric acid. The liquid obtained by B. Pelletier was at first regarded as a special acid and called *l'acide phosphatique—phosphatic acid.* U. J. J. Leverrier, indeed, suggested that this acid is a compound of phosphoric oxide and acid. As H. Davy expressed it in 1812, the acid *per deliquium* is a combination of phosphorous oxide and the aq. vap. of the air, and does not occur in air artificially dried. He added that the liquid is a mixture of phosphorous and phosphoric acids. P. L. Dulong, and

L. J. Thénard tried to show that the process of oxidation comes to a standstill when a certain proportion of phosphoric acid has been formed; but M. Pagels could not detect any such stationary stage—given sufficient time, the oxidation proceeds to the extreme limit. H. Davy's observation that ordinary phosphatic acid is a mixture of phosphorous and phosphoric acids was confirmed; and P. L. Dulong, and A. Sommer found that the liquid contains these two acids in the approximate proportion 1 : 4. H. Davy further observed that while solid phosphorus pentachloride reacts with water giving phosphoric acid, liquid phosphorus trichloride yields a syrupy liquid which crystallizes slowly on cooling, forming a substance with very singular properties and which "may be called *hydrophosphorous acid;* for it consists of pure phosphorous acid and water." H. Davy examined the properties of phosphorous acid; and its relations with the hypophosphorous and phosphoric acids were established by P. L. Dulong in 1816.

J. J. Berzelius made phosphorous acid by treating phosphorous oxide with water —a reaction studied by T. E. Thorpe and A. E. H. Tutton, *vide supra.* B. D. Steele obtained it by the action of iodine on hypophosphorous acid (*q.v.*) in the presence of mineral acids; and A. Besson, by heating the hemioxide with water in a sealed tube at 100°: $P_2O+O_2+3H_2O=2H_3PO_3$. Phosphorous acid is also produced by the action of hot dil. nitric acid on phosphorus; the objection to this process, said J. Corne, is the simultaneous production of phosphoric acid (*q.v.*), and this the more, the greater the conc. of the nitric acid. T. Salzer, and J. Philipp also reported that some hypophosphoric acid is produced at the same time. The early workers knew that the aq. soln. of phosphatic acid slowly decomposes, giving off phosphine, hence the faint smell like garlic. C. F. Schönbein mentioned that freshly prepared phosphatic acid contains a trace of nitric acid as well as ozone. A. Tamm also observed that some phosphorous acid is formed when phosphated steel is dissolved in nitric acid.

According to A. Oppenheim, phosphorous acid is formed when ordinary phosphorus is heated with conc. sulphuric acid in a sealed tube at 200°; some sulphur dioxide is simultaneously produced; and R. Rother, and A. L. Ponndorf observed its formation during the action of sulphur dioxide on hypophosphorous acid: $2H_3PO_2+SO_2=S+2H_3PO_3$. H. Schiff, R. M. Bird and S. H. Diggs, and O. J. Walker observed that some phosphorous acid is produced when a sat. soln. of cupric sulphate is allowed to act on yellow phosphorus while protected from air. Phosphorous acid is formed when hypophosphorous acid (*q.v.*) is oxidized by many metal oxides or salt soln. Thus, R. Engel observed this to occur during the action of that acid on palladium salts; and O. J. Walker on silver nitrate soln. According to A. Michaelis, and A. Besson, in H. Davy's mode of preparing phosphorous acid by the action of water on phosphorus trichloride, the reaction with water is quite a complicated one; the former imagined the reaction to involve the trio: (i) $PCl_3+H_2O=POCl_3+H_2$; (ii) $POCl_3+H_2=PCl_2(OH)+HCl$; and (iii) $PCl_2(OH)+2H_2O=H_3PO_3+2HCl$. A. Droquet recommended the following modification of H. Davy's process so as to avoid the special preparation of trichloride beforehand:

> A cylinder, 30 cms. long and 2·5 cms. in diameter, was one-quarter filled with phosphorus, and three-quarters with water, and then heated to the m.p. of the phosphorus. Chlorine was then passed into the cylinder by means of a tube reaching to the bottom. The chlorine fires the phosphorus, forming the trichloride which is decomposed by the superincumbent water. When the water is saturated with acid it is replaced by fresh water. The phosphorus must be kept in excess, or the pentachloride will be formed and the product accordingly be contaminated with phosphoric acid. J. Corne did not recommend this process because the formation of phosphoric acid cannot be avoided.

H. Grosheintz recommended rapidly passing the vap. of phosphorus trichloride at 60° in a current of dry air through two wash-bottles each containing 100 c.c. of water at 0°. In about 4 hrs., the contents of the first wash-bottle is a mush of crystals which can be drained, washed with ice-cold water, and dried in vacuo.

The mother-liquid is returned to the wash-bottle. T. Milobendzky and M. Friedman avoided the violent reaction of phosphorus trichloride and water in the preparation of phosphorous acid, by using conc. hydrochloric acid in place of water. Phosphorous acid is formed when several other phosphorous halides—PBr_3, PI_3, P_2I_4, etc.—are decomposed by water or by compounds which contain the elements of water; thus, A. J. Balard showed that it is formed by the action of water on the tribromide; L. Hurtzig and A. Geuther, by the action of phosphorous trichloride on oxalic acid heated in a flask fitted with a reflux condenser: $PCl_3+3H_2C_2O_4=H_3PO_3+3CO+3CO_2+3HCl$; and A. Geuther, by warming phosphorus trichloride with phosphoric acid: $PCl_3+3H_3PO_4=3HPO_3+H_3PO_3+3HCl$, or pyrophosphoric acid: $PCl_3+3H_4P_2O_7=6HPO_3+H_3PO_3+3HCl$—some red phosphorus may be formed at the same time.

D. Amato showed that some phosphorous acid is formed during the decomposition of spontaneously inflammable phosphine: $2PH_3+3O_2=2H_3PO_3$; H. J. van de Stadt studied the conditions favourable for this reaction—*vide supra*, phosphine. A. Besson found that phosphorous acid is formed when sulphuryl chloride reacts with phosphine; T. E. Thorpe and A. E. H. Tutton, when hydrochloric acid acts on phosphorous diamide: $HOP(NH_2)_2+2HCl+2H_2O=2NH_4Cl+H_3PO_3$; and A. Damoiseau, when yellow phosphorus acts on hydriodic acid: $2P+HI+3H_2O=H_3PO_3+PH_4I$.

H. Davy obtained crystals of phosphorous acid by evaporating the aq. soln. to a thin syrupy liquid, and cooling it; P. L. Dulong, and C. A. Wurtz evaporated the soln. until decomposition began, and allowed the mass to stand in vacuo for a few days. H. Rose, and C. F. Rammelsberg found that the thin syrup crystallized easier than the thick one. J. Thomsen evaporated the liquid with the temp. slowly rising to 180°, and found that the syrupy liquid on cooling crystallized in a few hours—often in a few minutes. If the liquid be seeded with a crystal of the acid, the cold or undercooled liquid crystallizes very quickly.

The white or grey mass consists of colourless crystals. According to J. Thomsen,[2] the fused acid has a sp. gr. 1·651 at 21·2°. L. Hurtzig gave 74° for the m.p., and J. Thomsen, 70·1°. For the m.p. of mixtures of phosphorous and phosphoric acids, *vide* Fig. 33. H. Davy found that the crystals, or conc. soln., decompose when heated into phosphine and phosphoric acid. P. Vigier represented the reaction by $4H_3PO_3=3H_3PO_4+PH_3$; and L. Hurtzig and A. Geuther found that some red phosphorus may be formed by rapidly heating the acid. N. R. Dhar found that the decomposition of phosphorous acid into phosphine and phosphoric acid is retarded by mild reducing agents. The mol. lowering of the f.p. was found by F. M. Raoult to be 2·39°; S. Arrhenius gave 2·6°–3·0°. A. Italiener measured the lowering of the f.p. and the raising of the b.p. of water by phosphorous acid, and found that if C represents the molar conc. of H_3PO_3 per litre, $\delta\theta$, the observed depression of the f.p., or the observed rise in the b.p.; k, the ionization constant assuming the molecule is H_3PO_3, and k_2, the constant on the assumption that the molecule is $(H_3PO_3)_2$; and i_1 and i_2 the corresponding association factors:

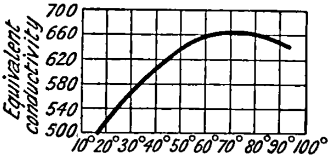


FIG. 33.—The Effect of Temperature on the Electrical Conductivity of Phosphorous Acid

	Freezing Solutions.					Boiling Solutions.			
C	1·186	0·539	0·296	0·148	C	0·976	0·488	0·244	0·122
$\delta\theta$	2·941°	1·538°	0·835°	0·455°	$\delta\theta$	0·51°	0·28°	0·16°	0·13°
k_1	20·98	25·96	28·18	30·70	k_1	5·23	8·74	6·56	10·56
i_1	1·128	1·143	1·515	1·650	i_1	0·969	1·063	1·215	1·972
k_2	41·96	51·92	56·36	61·40	k_2	10·26	11·48	13·12	21·30
i_2	2·256	2·286	3·030	3·210	i_2	1·938	2·126	2·430	3·944

With the lowering of the f.p., if the molecules are simply H_3PO_3, then in the less dil. soln. ionization occurs $H_3PO_3 \rightleftharpoons H^{\cdot}+H_2PO_3{}'$, and with the more dil. soln.,

$H_3PO_3 \rightleftharpoons 2H^{\cdot}+HPO_3''$. In that case, i should approximate to 2 with the less dil. soln., and exceed this value with the more dil. soln. This is not the case. With the raising of the b.p., very little ionization occurs on the assumption that the mols. are simply H_3PO_3. These contradictory conclusions are explained by assuming that at least in the conc. soln. there is an equilibrium condition, $2H_3PO_3 \rightleftharpoons (H_3PO_3)_2$; and that the complex mol. is partially ionized, $H_6P_2O_6 \rightleftharpoons H^{\cdot}+H_5P_2O_6'$, and $H_6P_2O_6 \rightleftharpoons 2H^{\cdot}+H_5P_2O_6''$. F. Guthrie found the eutectic temp. of acid and water to be $-1{\cdot}5°$. E. Cornec measured the lowering of the f.p. of a soln. of phosphorous acid when progressively neutralized by sodium hydroxide. As shown in Fig. 34, there are two breaks in the curve corresponding with the dibasicity of the acid. The results with phosphoric and hypophosphorous acids are shown in the same diagram for comparison. Analogous results were obtained with aq. ammonia in place of soda-lye. E. Cornec also measured the effect of the progressive neutralization of phosphorous acid with potassium hydroxide, and with aq. ammonia, the effect on the index of refraction of the soln. J. Thomsen gave 7·07 Cals. for the heat of fusion of phosphorous acid. The heat of formation of the crystallized acid, $(H_3,P,O_3)=227{\cdot}70$ Cals.; for the fused acid, 224·63 Cals.; and in aq. soln., 227·57 Cals. The heat of soln. of H_3PO_3 with an excess of water is 233 Cals., and of $H_3PO_3.3H_2O$, 152 Cals. The effect is zero with $H_3PO_3.400H_2O$. The heat of neutralization for $nH_3PO_{3aq.}+NaOH_{aq.}$ is 149 Cals. for $n=2$; 148 Cals. for $n=1$; 142 Cals. for $n=\frac{1}{2}$; and 96 Cals. for $n=\frac{1}{3}$. L. Amat gave $H_3PO_3+NaOH=NaH_2PO_3+H_2O_{solid}+25{\cdot}2$ Cals.; $H_3PO_3+2NaOH=Na_2HPO_3+2H_2O_{solid}+41{\cdot}6$ Cals.; and $H_3PO_{3aq.}+NaOH_{aq.}=NaH_2PO_{3aq.}+H_2O_{liquid}+14{\cdot}85$ Cals. P. A. Favre and J. T. Silbermann gave for the calorimetric eq. of phosphorous, phosphoric, and hypophosphorous acids, 2·91 : 4·36 : 1; and for the heat of oxidation, 140·394 Cals.

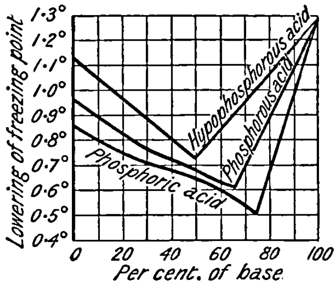
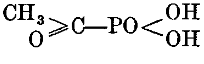


FIG. 34.—Effect of the Progressive Addition of some Phosphorous Acids to Sodium Hydroxide on the Lowering of the Freezing Point of the Solution.

F. Zecchini gave for the refraction eq. 26·04 with the μ-formula, and 15·17 with the μ^2-formula. O. Stelling measured the X-ray K-absorption spectrum of phosphorous acid, and of its salts and di-esters, and found that the results agree with the assumption that the phosphorus is tervalent with the solids, and tautomeric quinque- and ter-valent in soln. Phosphorous acid, the di-esters, methyl phosphorous acid, and ferric monopropyl phosphate have the structure $(RO)_2 : PO.H$; sodium diethyl phosphite, $(C_2H_5O)_2 : PO.Na$; silver diethyl phosphate, $(C_2H_5O)_2 : PO.OAg$; and monoacetyl phosphorous acid:



$$\left.\begin{matrix}CH_3\\O\end{matrix}\right\rangle C{-}PO\left\langle\begin{matrix}OH\\OH\end{matrix}\right.$$

A. Miolati and E. Mascetti measured the effect of progressive addition of sodium hydroxide and of ammonia on the sp. conductivity of phosphorous acid. W. Ostwald gave for the mol. conductivity, μ, at 25°, for soln. with a mol of the acid in v litres:

v	2	4	8	16	32	64	128	256	512	1024
μ	129	156	187	222	252	292	318	337	351	358

He represented the effect of temp. on the conductivity of normal soln. by Fig. 34. Observations were also made by A. Italiener, and A. Rosenheim and J. Pinsker. Comparing the results with the different phosphorus acids:

v		16	32	64	128	256	512	1024
μ	Phosphoric acid	124	156	195	240	279	317	341
	Hypophosphoric acid	184	199	222	246	275	304	370
	Phosphorous acid	222	257	292	318	337	351	358
	Hypophosphorous acid	245	281	312	335	352	361	367

A. Italiener gave for the hydrogen-ion conc. of soln. in which normality is represented by 37·84 grms. of the acid per litre:

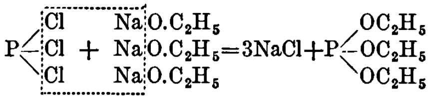
	N-	0·5*N*-	0·25*N*-	0·1*N*-	0·01*N*-	0·005*N*-
$[H^{\cdot}]$.	0·2337	0·1303	0·0931	0·04198	0·005984	0·002877

E. Blanc calculated for the ionization of constants of phosphorous acid $K_1=0\cdot05$, and $K_2=2\cdot4\times10^{-5}$. I. M. Kolthoff found that the first ionization constant K_1 increases from 0·016 in 0·001*M*-soln. to 0·062 in 0·1*M*-soln.; and the second ionization constant K_2, calculated from the $H^{\cdot}$-ion conc. of mixtures of a secondary phosphite with hydrochloric acid is $0\cdot0_67$ at 18°. The first stage of phosphorous acid titration may be conducted with methyl-orange as indicator using a comparison soln. with $p_H=3\cdot85$. A sharp end-point for the second stage is obtained with thymolphthalein as indicator. For the anodic oxidation of the phosphites, *vide infra*, perphosphates. P. Pascal studied the magnetic properties.

Analyses of the acid by H. Davy,[3] and H. Rose agree with the formula H_3PO_3. C. A. Wurtz found that the acid behaves as if it were bibasic. This makes it almost certain that two of the hydrogen atoms are similarly disposed in the molecule, and differently from the third hydrogen atom. Accordingly, A. Lieben, F. C. Palazzo and F. Maggiacomo, and L. Amat inferred that the phosphorus is quinquevalent and is associated with only two hydroxyl groups, $O=PH(OH)_2$, and not $P(OH)_3$, where the phosphorus would be tervalent. T. Graham supposed the acid to be tribasic; and in support of this, C. Zimmermann mixed a soln. of 6 mols of sodium hydroxide with one containing a mol of phosphorous acid, and, by adding absolute alcohol, precipitated a very viscid liquid, which was washed with alcohol until all the soda was removed. He said that considering the properties of the other alkaline phosphites it is not surprising that the viscid liquid cannot be crystallized. The soln. is strongly alkaline, and readily reduces soln. of silver salts. The ratio P : Na in the product was 1 : 3, and hence it was inferred that the soln. contained Na_3PO_3. L. Amat, however, was unable to verify this, for the only salt he could obtain was $OPH(ONa)_25H_2O$. V. Auger's attempts to prepare normal sodium phosphite, Na_3PO_3, by the action of excess of sodium ethoxide on an alcoholic soln. of phosphorous acid were unsuccessful, sodium hydrophosphite, Na_2HPO_3, being the only product. The dibasicity of the acid with respect to sodium hydroxide is in agreement with J. Thomsen's observations, who found that with 1, 2, and 3 mols of the sodium hydroxide per mol of phosphorous acid, respectively 14·8, 28·4, and 28·9 Cals. of heat were evolved, increasing the proportion of alkali beyond that corresponding with the formation of Na_2HPO_3 produces no marked thermal effect, indicating that no further reaction ensues. The results with pyrophosphoric, sulphuric, sulphurous, boric, carbonic, and other acids agree with the basicities usually assigned to them. Consequently, if the mol. wt. of an acid be known, its probable basicity can be deduced from observations on the heat evolved when it is neutralized step by step by means of an alkali. With metaphosphorous acid the results appear exceptional, for they indicate a monobasic acid; this is explained by assuming that the aq. soln. of metaphosphorous acid is unstable because it forms the ortho-acid. According to L. Amat, phosphorous acid is monobasic with methyl-orange; and dibasic with phenolphthalein and Porrior's sulphur-blue; and, according to A. Italiener, monobasic with methyl-orange, and dibasic with *p*-nitrophenol, and α-naphthophthalein. It exerts a slight reducing effect on *p*-nitrophenol.

Phosphorous oxide is considered to be the anhydride of phosphorous acid; but R. Reinitzer—*vide supra*, oxidation of phosphorus—raised the question whether this is really the case of the behaviour of the oxide when treated with water. It is not possible to say definitely whether the formula of phosphorous acid should be written $P(OH)_3$, or $OPH(OH)_2$, since the evidence from different sources appears contradictory when examined from different angles. The formation of the acid from phosphorus trichloride points to the formula $P(OH)_3$, and the dibasicity of the acid to the formula, $O:PH(OH)_2$. The latter formula appears the more probable.

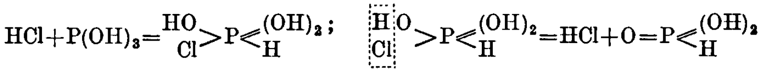
Under special conditions, the hydrogen directly attached to the phosphorus atom may have acidic properties, in the same way that the hydrogen of ammonia can be replaced by other radicles. Two isomeric *triethyl phosphites* have been prepared, by R. Railton, C. Zimmermann, A. E. Arbusoff, T. E. Thorpe and B. North; and by A. Michaelis and co-workers. The one obtained by the action of sodium ethoxide on phosphorus trichloride is supposed to be constituted $P(OC_2H_5)_3$, in accord with the equation:



$$\mathrm{P}\!\left\langle\begin{array}{l}\mathrm{Cl}\\ \mathrm{Cl}\\ \mathrm{Cl}\end{array}\right. + \begin{array}{l}\mathrm{Na\,O.C_2H_5}\\ \mathrm{Na\,O.C_2H_5}\\ \mathrm{Na\,O.C_2H_5}\end{array} = 3\mathrm{NaCl}+\mathrm{P}\!\left\langle\begin{array}{l}\mathrm{OC_2H_5}\\ \mathrm{OC_2H_5}\\ \mathrm{OC_2H_5}\end{array}\right.$$

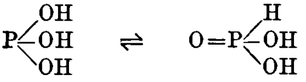
It is accordingly referred to as symmetrical ethyl phosphite. It is a liquid with a sp. gr. 0·9605 at 17°, it boils at 49° and 8–9 mm., and reduces soln. of mercuric chloride. The other is obtained by the action of ethyl alcohol on phosphorous oxide, or by treating lead phosphite with ethyl iodide. It is a liquid of sp. gr. 1·028 at 21°; it boils at 198° and 760 mm.; and does not reduce soln. of mercuric chloride. It is referred to as unsymmetrical ethyl phosphite, and is supposed to be constituted like ordinary phosphorous acid, $O=P(C_2H_5)(OC_2H_5)_2$. Phosphorous acid is prepared by a method analogous to that employed for the symmetrical acid. Hence, it is assumed that while there is a simple metathecal change when sodium ethoxide and phosphorus trichloride react, yet, in the case of water and phosphorus trichloride, it is assumed that there is an intramolecular change resulting in the formation of unsymmetrical phosphorous acid and an increase in the valency of the phosphorus.

A. E. Arbusoff assumed that symmetrical phosphorous acid is first formed: $PCl_3+3H_2O=P(OH)_3+3HCl$, where the phosphorus remains tervalent. P. Pascal's observations on the magnetic properties of the phosphites agree with the formula $P(OH)_3$. The great tendency of the compounds of tervalent phosphorus to form addition products has been emphasized by the work of A. E. Arbusoff, P. Schützenberger, C. Risler, and L. Lindet; but not so with the quinquevalent phosphorus compounds. Accordingly, A. E. Arbusoff assumes that the symmetrical phosphorus acid forms a complex $P(OH)_3HCl$ with hydrogen chloride produced by the reaction. This involves the restoration of the two latent valencies of phosphorus; the complex is unstable, then breaks down into unsymmetrical phosphorous acid without changing the valency of the phosphorus:



$$\mathrm{HCl+P(OH)_3=\begin{array}{c}HO\\ Cl\end{array}\!>\!P\!<\!\begin{array}{l}(OH)_2\\ H\end{array};\quad \begin{array}{c}H\\ Cl\end{array}\begin{array}{c}O\\ \ \end{array}\!>\!P\!<\!\begin{array}{l}(OH)_2\\ H\end{array}=HCl+O=P\!<\!\begin{array}{l}(OH)_2\\ H\end{array}}$$

This recalls the parallel case of the addition of hydrogen halides to the unsaturated hydrocarbons observed by A. P. Eltekoff. As in the case of sulphurous and nitrous acids, the facts can also be explained by assuming the desmotropic change:



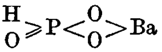
$$\mathrm{P}\!\left\langle\begin{array}{l}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\end{array}\right. \rightleftharpoons \mathrm{O{=}P}\!\left\langle\begin{array}{l}\mathrm{H}\\ \mathrm{OH}\\ \mathrm{OH}\end{array}\right.$$

Symmetrical Acid. Unsymmetrical Acid.

This view is supported by A. D. Mitchell's observations on the action of water on phosphorus trichloride (*q.v.*), and by O. Stelling's observations on the K-absorption X-ray spectrum. A. Rosenheim and A. Italiener found that the depression of the f.p., and the elevation of the b.p. of aq. soln. agree with the assumption that phosphorus acid has the constitution $H_4(P_2O_6H_2)$ in complete analogy with $H_4(P_2O_7)$ for pyrophosphoric acid. There is thus a complete set of ions:

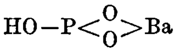
$PO_4^{\cdots}$	$HPO_3^{\cdot\cdot}$	$H_2PO_2^{\cdot}$	H_3PO	PH_4'
Phosphate.	Phosphite.	Hypophosphite.	Phosphine oxide.	Phosphonium.

G. Oddo discussed this reaction as an example of what he calls *mesoidria, i.e., mesohydry.* L. Lendle, and G. Schick inferred that barium phosphite exists in isomeric forms because of the difference in the reducing properties of the phosphites prepared at high and at low temp. The low temp. form was said to be the most active, and to it was attributed an aldolic structure; while the enolic structure was assigned to the less active form prepared at the high temp.:



$${}^{H}_{O}{\geqslant}P{<}^{O}_{O}{>}Ba$$

Aldolic barium phosphite.



$$HO{-}P{<}^{O}_{O}{>}Ba$$

Enolic barium phosphite.

The inversion from one form to the other was supposed to explain the maximum attained by the conductivity curve, Fig. 33. H. Gorke showed that there is no need for this hypothesis to explain the facts. The salt prepared at the low temp. may have a trace of impurity, say barium hydroxide, which accelerates the reduction, and that prepared at the higher temp. may be an acid salt or contain a trace of phosphoric acid which retards the reduction. H. Burgarth, H. Remy, and T. M. Lowry discussed the electronic structure of phosphorous acid—*vide supra,* phosphoric acid.

P. Schulz found that phosphorous acid or the phosphites act on the nerve centres and abdominal glands. The thermal decomposition of phosphorous acid into phosphine and phosphoric acid: $4H_3PO_3=3H_3PO_4+PH_3$—*vide infra,* phosphites—was found by N. R. Dhar to be hindered by mild reducing agents. L. Dusart said that while **hydrogen** has no reducing action on phosphorous acid, hydrogen *in statu nascendi* reduces the acid to phosphine. The crystallized acid deliquesces in air producing a colourless liquid. The conc. aq. soln., said C. A. Wurtz, should be protected from **air** on account of their tendency to take up **oxygen**; but J. L. Gay Lussac observed no tendency on the part of the phosphites to absorb oxygen from the air. R. Luther and J. Plotnikoff found that the reaction $H_3PO_3+\frac{1}{2}O_2=H_3PO_4$ is immeasurably slow in the absence of iodine as catalyst—either in darkness or in light; but in the presence of the catalyst iodine, reaction proceeds in light. The reactions involved are (i) $2HI+O=I_2+H_2O$, a change which is slow in darkness, but rapid in light; and (ii) $H_3PO_3+H_2O+I_2=H_3PO_4+2HI$, a reaction which takes place rapidly, and is not affected by light. W. Omeliansky showed that the organism which converts nitrates into nitrites does not oxidize sodium phosphite or sulphite. H. Wieland and A. Wingler found that aq. soln. of phosphorous acid do not absorb oxygen, but do so in presence of palladium black, phosphoric acid resulting. Charcoal does not act like palladium. Soln. with anhydrous, dry palladium black does not cause the absorption of oxygen in dry ethereal soln., whereas, on admitting traces of water, reaction proceeds rapidly. Similarly, palladium black, *p*-benzoquinone, and phosphorous acid do not interact in absence of water. It is therefore concluded that the reducing action of phosphorous acid is due, not to its absorption of oxygen, but to the loss of hydrogen from a *hydrate,* which is the active form: $O:PH(OH)_2\rightarrow PH(HO)_4\rightarrow 2H+O:P(OH)_3$. A. Italiener measured the solubility of the acid in **water,** and expressing the results in grams of H_3PO_3 and P_2O_3 per 100 grms. of soln.:

	0°	20·25°	25·4°	30°	35°	39·4°
H_3PO_3 . .	75·58	82·00	82·64	84·12	85·00	87·42
P_2O_3 . .	50·7	55·00	55·44	56·43	57·02	58·64

The solubility is thus very great, and in the interval between 0° and 40°, there is no sign of the formation of a definite hydrate. H. Rose observed no development of hydrogen when the phosphites are boiled with **alkali hydroxides.** A. Italiener studied the titration of phosphorous acid with alkali-lye.

H. Wieland and A. Wingler found that **bromine** does not react in dry ethereal soln. with phosphorous acid; but the reaction is rapid if a trace of water be present.

According to O. Ordinaire, when a mol of phosphorous acid is heated with 4 gram-atoms of bromine, there are formed hydrogen bromide and not phosphoric acid, but rather *monobromophosphorous acid* as a deliquescent, crystalline substance, soluble in ether; **chlorine** at 100° acts similarly, producing *monochlorophosphorous acid.* G. Gustavson found that when a mixture of phosphorous acid and bromine is heated in a sealed tube to 100°, phosphoric acid is produced: with 2 gram-atoms of bromine per mol. of phosphorous acid, metaphosphoric acid is formed: $H_3PO_3+Br_2=HPO_3+2HBr$; and with 6 gram-atoms of bromine to 4 mols of the acid, orthophosphoric acid is formed: $4H_3PO_3+3Br_2=PBr_3+3HBr+3H_3PO_4$. W. Manchot and F. Steinhauser observed that bromine in the presence of hydrochloric or sulphuric acid does not oxidize phosphorous acid completely, but in the presence of sodium hydrocarbonate, immediate oxidation occurs, showing that sodium hypobromite is probably the active agent. I. M. Kolthoff found that the oxidation of phosphorous acid by bromine goes very slowly in conc. acid soln., but rapidly when the soln. is buffered to an acidity of $p_{\mathrm{H}}=4$ to 5. A. Sommer discussed the oxidation of phosphorous acid by bromine, obtaining hydrobromic acid as a by-product: $Br_2+H_3PO_3+H_2O=2HBr+H_3PO_4$, G. Gustavson observed similar reactions with **iodine**: with a small proportion of iodine, metaphosphoric acid and phosphorus diiodide are produced; with a mol of the acid and a gram-atom of iodine, some iodine remains unattacked; and with double the proportion of acid: $8H_3PO_3+5I=6H_3PO_4+2HI+PH_4I+PI_2$. According to J. Thomsen, chlorine-water, bromine-water, or iodine-water oxidize the acid to phosphoric acid, and the oxidation is fastest with bromine water. E. Rupp and A. Finck found that soln. of phosphorous acid react only slowly with iodine, but if the liberated hydriodic acid be neutralized by sodium carbonate present in the soln., the oxidation proceeds more quickly. W. Federlin said that the oxidation of phosphorous acid by iodine proceeds very slowly in acidic soln., and is a reaction of the second order. According to B. D. Steele, two reactions of essentially different character occur between iodine and phosphorous acid, one of which preponderates in more strongly acid soln., and the other, in the presence of feeble acids, such as acetic and boric acids. The former of these reactions is catalytically accelerated by the presence of hydrogen ions, and the velocity is proportional to the concentration of phosphorous acid (or of the phosphorous ion) and to the square root of the concentration of the iodine. This is taken to mean that reaction takes place between phosphorous acid mols. (or ions) and iodine atoms, the latter being supplied in extremely small, but sufficient, quantity by the dissociation of the iodine mols. There is a slight apparent retardation of the reaction velocity by the iodine. The second reaction occurs in the presence of salts, such as sodium acetate, bicarbonate, or biborate, and it is very complex; it is accelerated by the presence of phosphorous acid or of sodium acetate, and retarded by the presence of iodine or of potassium iodide. A. D. Mitchell showed that the reaction with iodine and phosphorous acid involves the reversible transformation of two forms of phosphorous acid, the α- or normal form and a β-form: α-$H_3PO_3=\beta$-H_3PO_3; and it involves the I_2-molecule, and the I_3'-ion: α-$H_3PO_3+I_2+H_2O=2HI+H_3PO_4$, and β-$H_3PO_3+I_2+N_2O=H_3PO_4+2H^{\cdot}+I_3'$. The $H^{\cdot}$-ions repress the former, and accelerate the latter, but this acceleration is probably only indirect, and due to the acceleration of the equilibrium between the two forms of the acid, as in the case of hypophosphorous acid. The mechanism of the repressing effect has not been elucidated. The reaction was also studied by E. I. Orloff, A. Brukl and M. Behr, M. Boyer and M. Bauzil, and T. F. Buehrer and O. E. Schupp. C. A. Wurtz found that **hypochlorites** oxidize phosphorous acid to phosphoric acid, and H. Davy observed that **hypochlorous acid** acts in the same way, and that when the acid is warmed with **iodic acid**, iodine and phosphoric acid are formed, but he obtained what he regarded as a compound of phosphorous and iodic acids—*phosphitoiodic acid*—by mixing aq. soln. of the two acids. The yellow product could be sublimed. G. S. Sérullas doubted the existence of this as a chemical individual, although

C. W. Blomstrand made a number of analogous complex acids. D. Vitali found that phosphorous acid reduces **iodates** with the liberation of iodine which is then redissolved as hydriodic acid—the **chlorates** and **bromates** are not reduced by the acid. A. Brukl and M. Behr determined phosphorous acid by determining the iodine liberated by it from phosphorous acid.

F. Wöhler represented the action which occurs when **sulphurous acid** is warmed with phosphorous acid: $3H_3PO_3+H_2SO_3=3H_3PO_4+H_2S$; and the hydrogen sulphide then reacts with the excess of sulphurous acid, forming pentathionic acid and sulphur; and A. Cavazzi symbolized the reaction at 60°–70° by $2H_3PO_3+H_2SO_3=2H_3PO_4+S+H_2O$. C. F. Schönbein mentioned that the product of the reaction quickly decolorizes a soln. of indigo blue; and L. Maquenne said that some hyposulphurous acid is formed at an intermediate stage in the reduction of the sulphurous acid to sulphur. C. A. Wurtz found that hot conc. **sulphuric acid** oxidizes phosphorous to phosphoric acid. According to R. H. Adie, anhydrous phosphorous acid dissolves quietly in conc. sulphuric acid without forming an insoluble compound. The mixture when warmed gives off sulphur dioxide, and contains phosphoric acid only. When anhydrous phosphorous acid was dropped into **sulphur trioxide,** there was a great development of heat, accompanied by the formation of sulphur dioxide and some sulphur. A blue, oily compound separated out in small quantity from the trioxide, which was itself coloured a fine indigo-blue. At the high temp. produced by the reaction, the phosphorous acid reduced some of the trioxide to sulphur, which dissolved in the trioxide to form blue sulphur sesquioxide. The phosphorous acid is almost completely oxidized, by the reduction of the trioxide in the cold, to sulphur dioxide, and, if warm, to sulphur dioxide and sulphur, forming the compound $H_2PO_4,3SO_3$, or $(SO_3H)PO_4$, **sulphonyl phosphate.** W. Federlin found that the reaction between **potassium persulphate** and phosphorous acid is very slow, but in the presence of hydriodic acid, the reaction proceeds with measurable velocity —presumably in two stages: (i) the oxidation of the iodide to iodine by the persulphate, and (ii) the oxidation of the phosphorous acid by the iodine. Iron and copper salts accelerate the reaction. The effect of varying the conc. of the reaction constituents, and the temp. was examined. A. Gutbier found that **selenious acid** is reduced to selenium, and **tellurous acid** to tellurium. H. Davy found that phosphorous acid is oxidized by **nitric acid** to phosphoric acid; A. Joly, that the acid reacts with **metaphosphoric acid,** forming pyrophosphoric acid and hydrogen diphosphide; and L. Amat, that the acid forms hydrogen diphosphide when heated with **phosphorous oxide.** A. Naquet observed that when the acid is heated with **phosphorus trichloride** it forms phosphorous oxide, but K. Kraut represented the reaction: $PCl_3+4H_3PO_3=3H_3PO_4+2P+3HCl$; A. Gautier said that with the crystallized acid and phosphorus trichloride in a sealed tube at 79°, an oxyhydride is formed: $11PCl_3+27H_3PO_3=4P_4HO+11H_4P_2O_7+33HCl$; at 100°, red phosphorus is produced: $3P_4HO+PCl_3+3H_3PO_3=3H_3PO_4+3HCl+13P$; and at 170°, $3PCl_3+7H_3PO_3=4P+3H_4P_2O_7+9HCl$; A. Besson represented the reaction with a conc. soln. of the acid: $PCl_3+H_3PO_3=3HCl+P_2O_3$, and $2P_2O_3=P_2O+P_2O_5$; while A. Geuther said that the reaction is best symbolized: $H_3PO_3+2PCl_3=3P(OH)Cl_2$; $3P(OH)Cl_2=3POCl+3HCl$; $3POCl=P_2O_3+PCl_3$; and $3H_3PO_3+P_2O_3=3H_3PO_4+2P$. He also represented the action of **phosphorus pentachloride**: $H_3PO_3+3PCl_5=PCl_3+3POCl_3+3HCl$—the phosphorus trichloride reacts as just indicated, forming red phosphorus; while the **phosphoryl chloride** reacts: $3POCl_3+2H_3PO_3=3HPO_3+2PCl_3+3HCl$. E. Chambon found that **phosphoryl dichlorobromide** does not produce phosphorus dichlorobromide, but a mixture of phosphorus trichloride and tribromide as well as hydrogen chloride, and metaphosphoric and orthophosphoric acids. B. Grützner found that phosphorous acid reacts with **antimony trioxide,** forming **antimonyl phosphite,** and with **bismuth hydroxide,** forming bismuth phosphite.

T. E. Thorpe and B. North prepared diethyl phosphite, $P(OH)(OC_2H_5)_2$—*vide* *supra.*—by the action of well-cooled phosphorous acid and **alcohol**; the reaction with different alcohols was examined by A. Sachs and N. Levitsky; with **glycerol, glycol,** and **mannite,** by P. Carré; **acetyl chloride,** by N. Menschutkin; **acetic anhydride,** by V. Wedensky; **diazoethane,** by F. C. Palazzo and F. Maggiacomo; etc. According to A. Italiener, it has a slight reducing action on the indicator, *p*-**nitrophenol.**

According to C. F. Rammelsberg, soln. of **copper salts** are decolorized by an excess of phosphorous acid, and cuprous oxide is precipitated; with the copper salt in excess, copper is precipitated: $3H_3PO_3+CuSO_4+3H_2O=3H_3PO_4+H_2SO_4+Cu+2H_2$. According to L. Vanino, if a 10 per cent. aq. soln. of copper sulphate be mixed with phosphorous acid soda-lye produces a turbidity which clears up when more of the alkali-lye is added. M. Major said that the reaction between copper salts and phosphorous acid is completed with the development of hydrogen; and no intermediate stage can be observed in the reduction to the metal. A. Sieverts, and M. Major represented the reaction: $CuSO_4+H_3PO_3+H_2O=Cu+H_3PO_4+H_2SO_4$; they found that cupric chloride yields cuprous chloride. C. A. Wurtz, A. J. Balard, and O. von der Pfordten found that **silver salts** oxidize phosphorous to phosphoric acid with the precipitation of the metal; if the silver salt is in excess, C. F. Rammelsberg represented the reaction: $AgNO_3+H_2O+H_3PO_3=Ag+H+HNO_3+H_3PO_4$. L. Vanino found that silver salts do not behave like copper salts when treated as indicated above. A. Sieverts, and M. Major could detect no intermediate product of the reduction, and no hydrogen was developed; he represented the reaction: $2Ag_3PO_4+3NaH_2PO_3+3H_2O=6Ag+2H_3PO_4+3NaH_2PO_4$. A. Sieverts found that soln. of silver oxide in potassium cyanide soln. are not reduced by phosphorous acid. A. J. Balard, and C. A. Wurtz observed the reduction of **gold salts** to the metal by phosphorous acid; A. Sieverts, and M. Major represented the reaction: $2AuCl_3+3H_3PO_3+3H_2O=2Au+3H_3PO_4+6HCl$. L. Vanino found that with **alkaline earth salts** clear soln. are obtained by the treatment he employed for copper salts—*vide supra.* C. A. Wurtz, and A. J. Balard found that **mercuric salts** are reduced by phosphorous acid to mercury; if an excess of mercuric chloride is used, mercurous chloride is precipitated. C. Montemartini and U. Egidi represented the reaction: $2HgCl_2+H_3PO_3+H_2O=2HgCl+2HCl+H_3PO_4$, and thus considered it to be of the third order, but the velocity constants were not concordant, and they attributed the discrepancy to some unrecognized disturbance; J. B. Garner and co-workers did not succeed in clearing up the difficulty; then G. A. Linhart showed that the reaction is of the first order with respect to mercuric chloride, and the whole reaction possibly occurs in two stages: $HgCl_2+H_3PO_3=HCl+HgCl+H_2PO_3$, followed by $2H_2PO_3+H_2O=H_3PO_4+H_3PO_3$. The latter reaction is much more rapid than the former. The reaction is accelerated by acids. The reaction was also studied by A. Linhart and E. Q. Adams, N. R. Dhar, W. Federlin, and B. D. Steele. According to A. D. Mitchell, there is first a reversible reaction between the ordinary α-form of phosphorous acid and a β-form: $\alpha\text{-}H_3PO_3 \rightleftharpoons \beta\text{-}H_3PO_3$, which is accelerated in both directions by $H^{\cdot}$-ions and $\beta\text{-}H_3PO_3+HgCl_2+H_2O=Hg+H_3PO_4+2HCl$, followed by the instantaneous reaction $Hg+HgCl_2=Hg_2Cl_2$. In the absence of extraneous Cl'-ions initially, the reaction $HgCl'+\alpha\text{-}H_3PO_3+H_2O=H_3PO_4+Hg+2H^{\cdot}+Cl'$ preponderates until the accumulation of Cl'-ions reduces it to a lower order of magnitude. With low conc. of $H^{\cdot}$-ions (*i.e.* in the presence of an excess of sodium acetate) another instantaneous reaction occurs; and yet another, $HgCl_2+\alpha\text{-}H_3PO_3 \rightleftharpoons X+H^{\cdot}+Cl'$, where X represents an intermediate compound. The resultant reaction is therefore compounded of a side and consecutive reactions. The reaction was also studied by R. M. Purkayostha and N. R. Dhar. B. Grützner observed that colloidal **alumina** forms a basic phosphite when treated with phosphorous acid; and that **chromic salts** are not reduced to an appreciable extent by phosphorous acid, and chromic hydroxide dissolves in the acid. N. R. Dhar found the reaction to be unimolecular with respect to chromic acid when an excess of phosphorous acid is present. C. A. Wurtz, and A. J. Balard found that **chromates** are quickly reduced by phosphorous acid; W. Gibbs found that phosphorous acid forms complex salts with **molybdenum trioxide**, and with **tungsten trioxide**. A. J. Balard, and C. A. Wurtz found that phosphorous acid reduces the **permanganates**. L. Amat found the speed of the reduction proceeds more quickly the more conc. the soln., the more acidic the liquid, and the higher the temp. The reaction is incomplete at ordinary temp. O. Kühling represented the reaction: $3H_3PO_3+2KMnO_4=3H_3PO_4+2MnO_2+K_2O$; and J. Pinsker studied the reaction. According to L. Vanino, **ferrous and ferric salts**, like copper salts, form clear soln. when treated as indicated above. B. Grützner found that freshly precipitated ferric hydroxide forms ferric phosphite when treated with phosphorous acid. M. Major found that at 50°, **nickel** is dissolved by phosphorous acid. A. Sieverts found that **cobalt salts** and **nickel salts** are not reduced by phosphorous acid; B. Grützner showed that cobalt and nickel hydroxides dissolve in the acid without reduction; and L. Vanino, that soln. of cobalt and nickel sulphates behave like those of copper sulphate—*vide supra*. A. Sieverts found that **palladium salts** are reduced in the cold by phosphorous acid.

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§ 18. The Phosphites

C. A. Wurtz [1] said that the affinity of phosphorous acid for the bases is small, but they have a great tendency to form double salts. Phosphorous acid unites with bases and metal-oxides, forming **phosphites.** There are two types of salts—*primary phosphites*, MH_2PO_3; and *secondary phosphites*, M_2HPO_3, where M denotes a monad. C. Zimmerman reported a *tertiary phosphite*, Na_3PO_3, but, according to L. Amat, C. Zimmermann mistook normal sodium phosphite, Na_2HPO_3, for the tertiary salt. The alkali and calcium phosphites are soluble in water, the other salts are but sparingly soluble. Many of the less soluble phosphites are soluble in an excess of the acid, probably owing to the formation of soluble double salts. The phosphites have been specially studied by C. A. Wurtz, H. Rose, C. F. Rammelsberg, L. Amat, J. L. Gay Lussac, etc. The double phosphites are soluble in water. The phosphites—solid or in aq. soln.—are fairly stable in air at ordinary temp., but, when heated, they decompose with the evolution of hydrogen or phosphine, and the formation of ortho- or pyro-phosphate—*e.g.* $5PbHPO_3 = Pb_2P_2O_7 + Pb_3(PO_4)_2 + PH_3 + H_2$. Boiling the phosphite with alkali-lye furnishes hydrogen: $Na_2HPO_3 + NaOH = Na_3PO_4 + H_2$, but with dil. soln. no appreciable amount of hydrogen is evolved.

A. F. de Fourcroy and L. N. Vauquelin,[2] and H. Rose prepared **ammonium phosphite,** $(NH_4)_2HPO_3.H_2O$, by saturating an aq. soln. of phosphorous acid with ammonia, and evaporating the soln. to a syrupy consistence when it yields large "four-sided prisms with quadrilateral summits." C. A. Wurtz evaporated the soln. over conc. sulphuric acid, and analyzed the product. G. Lemoine obtained the salt as a by-product in the action of ammonium sulphide on phosphorus sesquisulphide. The salt is very deliquescent. When the salt is kept in vacuo, or when the soln. is evaporated at 100°, C. A. Wurtz found that it lost its water of crystallization along with some ammonia; and H. Rose, and A. F. de Fourcroy and L. N. Vauquelin reported that when the salt is heated it loses ammonia, leaving hydrated phosphorous acid as a residue, which is decomposed at a higher temp. into phosphine and phosphoric acid. L. Amat found that when kept for 24 hrs. in vacuo, the monohydrate becomes anhydrous: $(NH_4)_2HPO_3.H_2O = (NH_4)_2HPO_3 + H_2O$. The anhydrous salt was also made by L. Amat by passing ammonia over the hydrophosphite at 100°; and T. E. Thorpe and A. E. H. Tutton obtained it as a by-product along with diamidophosphorous acid, when ammonia acts on phosphorous acid. According to L. Amat, the white powder has a dissociation press. of 15 mm. at 75°. H. Stamm found that the salt is precipitated from its conc. aq. soln. by ammonia. L. Amat, and A. P. Sabanéeff made **ammonium hydrophosphite,** $(NH_4)H(HPO_3)$, by neutralizing a soln. of phosphorous acid with ammonia, using methyl-orange as indicator. The soln. is evaporated until a drop crystallizes when cooled. The evaporation must be carefully performed or the salt will decompose. It is also formed when normal ammonium phosphite is heated to 100°, or kept in vacuo. A. P. Sabanéeff said that the salt is isomeric with hydroxylamine hypophosphite. According to H. Dufet, the crystals are monoclinic prisms with the axial ratios $a:b:c = 0{\cdot}7616:1:0{\cdot}9618$, and $\beta = 103° \, 6\frac{3}{4}'$; the optic axial angle $2H_a = 13° \, 50'$. L. Amat said that the salt is stable at 100°, but melts at 123°; while A. Sabanéeff said that it melts with partial decomposition at 120°, and that the presence of a trace of water lowers the m.p. According to L. Amat, the molten salt begins to decompose at 145° with the loss of ammonia, but not phosphine; when heated still more, phosphine is also given off, and phosphorous acid remains. The salt is very soluble in water, since 100 grms. of water dissolve 171 grms. of salt at 0°; 190 grms. at 14·5°; and 260 grms. at 31°. Very little ammonia is absorbed by the salt at ordinary temp., but at 100°, ammonia is freely absorbed, forming the normal phosphite. A. P. Sabanéeff said that the salt does not reduce alkaline copper salts in the cold, but it gives a precipitate with barium chloride. J. Zawidzky studied the rate of the isomeric change of the alkyl phosphites.

According to K. A. Hofmann and V. Kohlschütter, **ammonium hydroxylamine phosphite,** $(NH_4)(NH_3OH)(HPO_3)$, is obtained by neutralizing phosphorous acid with ammonia, then adding four times the quantity of ammonia and two mol. proportions of hydroxylamine hydrochloride to one of the acid; after remaining one hour, the soln. is precipitated with alcohol and the product recrystallized from absolute alcohol. It is also obtained by heating normal ammonium phosphite with a soln. of hydroxylamine hydrochloride in absolute ethyl alcohol and dissolving out the excess of hydroxylamine hydrochloride from the product by warming it with methyl alcohol. It crystallizes in slender, white needles, and at once reduces Fehling's soln. and ammoniacal silver nitrate. A. P. Sabanéeff said that this salt is isomeric with ammonium hydrophosphate. K. A. Hofmann and V. Kohlschütter made **hydroxylamine phosphite,** $(NH_3OH)_2(HPO_3)$, by mixing an aq. soln. of disodium phosphite with 3 mol. proportions of hydroxylamine hydrochloride, and after crystallizing out the sodium chloride by evaporation in vacuo over sulphuric acid, the gummy residue is crystallized from absolute alcohol; it crystallizes in long, colourless needles, burns, when heated, with a green flame and evolution of hydrogen phosphide, and quickly reduces Fehling's soln. and ammoniacal silver nitrate. A. P. Sabanéeff said that **hydroxylamine hydrophosphite,** $(NH_3OH)H(HPO_3)$, is isomeric with ammonium dihydrophosphate. He obtained normal **hydrazine phosphite,** $(N_2H_6)(HPO_3)$, from barium phosphite and hydrazine sulphate; it is very hygroscopic, and melts at 36°. It is isomeric with ammonium hydrogen amidophosphate, which decomposes at 120° and melts at 305°. He also made **hydrazine hydrophosphite,** $H(HPO_3)_2N_2H_6(H.HPO_3)_2$, obtained from hydrazine sulphate and barium hydrogen phosphite, melting at 82° without decomposition. It is isomeric with ammonium hypophosphate, $(NH_3)_2H_4P_2O_6$, which melts at 170°.

A. Rosenheim and W. Reglin[3] prepared **lithium hydrophosphite,** $Li_2HPO_3.H_2O$, in 4-sided plates, from a soln. of equimolar parts of lithium carbonate and phosphorous acid concentrated for crystallization on a water-bath. The salt has a negative temp. coeff. for the solubility, S grms. of $Li_2HPO_3.H_2O$, in 100 grms. of soln.:

	0°	25°	30°	35°	40°	45°	50°	61°	98°
S .	9·07	7·47	7·07	6·82	6·64	6·29	6·09	5·75	4·24

the solid phase was always the monohydrate. The $H^{\cdot}$-ion conc. of a N-soln. at 20° is $p_H=8{\cdot}14$, or $[H^{\cdot}]=7{\cdot}34\times10^{-9}$ grms. per litre. The lowerings of the f.p. with 0·4014, 0·9095, and 1·4076 grm. of the monohydrate in respectively 19·243, 19·33, and 19·41 grms. of water were 0·820°, 1·7550°, and 2·710°, respectively corresponding with the factors $i=2{\cdot}37$, 2·25, and 2·25, thus showing that the salt is probably associated to $(Li_2HPO_3)_2$ in soln. The eq. electrical conductivities, λ, for a mol of the salt in v litres of water at 25°:

v . . .	32	64	128	256	512	1024
λ . . .	68·1	72·6	76·4	82·1	86·0	102·4

There is no evidence of adsorption when the salt is crystallized from a conc. soln. of lithium hydroxide. L. Amat obtained easily soluble **lithium dihydrophosphite,** LiH_2PO_3—from a soln. of lithium carbonate or hydroxide neutralized with phosphorous acid, using methyl-orange as indicator. C. Zimmermann's report of the preparation of **sodium orthophosphite,** Na_3PO_3, has already been described. P. L. Dulong, H. Dufet, and C. A. Wurtz prepared **sodium hydrophosphite,** $Na_2HPO_3.5H_2O$, by neutralizing a soln. of phosphorous acid with sodium carbonate, and evaporating the liquid for crystallization. A. Italiener recommended using α-naphtolphthalein as indicator, and evaporated the syrupy liquid over conc. sulphuric acid. The analysis of the long, acicular crystals so obtained corresponded closer with $Na_2HPO_3.5{\cdot}5H_2O$, than with the pentahydrate. A. F. de Fourcroy and L. N. Vauquelin appear to have obtained this salt from the so-called *acide phosphatique*—*vide supra.* P. L. Dulong said that the crystals are rhombohedra inclined to the cubical form ; and H. Dufet gave for the axial ratios of the rhombic bipyramidal crystals $a:b:c=0{\cdot}6998:1:0{\cdot}7813$. The index of refraction for Na-light is $\beta=1{\cdot}4434$; the birefringence is positive and feeble ; the optic axial angle $2V=43°\ 16'$ for Li-light ; 44° 7′ for Na-light ; and 44° 45′ for Tl-light, and there is a rise of about 10′ for a degree rise of temp. H. Rose said that the crystals decompose when heated, giving off hydrogen. L. Amat gave 53° for the m.p. ; and the salt is dehydrated at 150°. The anhydrous salt is formed by keeping the pentahydrate in vacuo, or over conc. sulphuric acid, or else heating it to 120°. K. Kraut said that when heated in a current of air, a little phosphine is given off at 200°–250°, and when the residue is digested in water, a little red phosphorus remains undissolved. F. M. Raoult said that the f.p. is lowered 0·327° by the dissolution of a gram of the anhydrous salt in 100 c.c. of water ; and the mol. lowering of the f.p. is 41·2°. J. Thomsen measured the heat of neutralization of phosphorous acid and sodium hydroxide—*vide supra.* L. Amat gave for the heat of formation $H_3PO_3+2NaOH=Na_2HPO_3+2H_2O_{solid}+41{\cdot}6$ Cals. and for the heat of soln., 4·6 Cals. at 13·5°. A. Italiener, and I. Müller gave 10° for the hydrogen-ion conc. The solubility of the salt in water is greater than that of phosphorous acid ; expressing the results in grams of $Na_2(HPO_3)$ per 100 grms. of soln., A. Italiener found :

	0°	20°	25·2°	29·9°	38°	42·7°
Solubility .	80·72	81·16	82·21	84·96	91·44	93·68

The curve shown in Fig. 35 is not inconsistent with the existence of another hydrate with a transition point near 20°, but none was found. E. Blanc estimated that in 0·0075*N*-soln., 0·021 per cent. of sodium phosphite is hydrolyzed. A. Italiener gave for the H-ion conc. [H$^{\cdot}$] 10^{-9} grm. per litre at 20°. H. Stamm found that the salt is precipitated by ammonia from its conc. aq. soln. P. L. Dulong, H. Rose, and C. A. Wurtz prepared **potassium phosphite,** $K_2(HPO_3)$, by neutralizing phosphorous acid with potassium hydroxide. H. Rose found the syrupy liquid crystallized when kept in vacuo. C. A. Wurtz said the salt can be dried at 280° without decomposition. P. L. Dulong said that the salt is deliquescent in air, and insoluble in alcohol. According to A. Gutmann, a cold or boiling soln. of sodium thiosulphate does not act on sodium or potassium phosphite—*vide* the arsenites. N. N. Mittra and N. R. Dhar found that the reaction with mercuric chloride and sodium phosphite as primary reactions is hastened by the simultaneous reaction of mercuric chloride with sodium arsenite or arsenious acid.

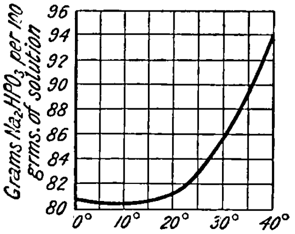

FIG. 35.—The Solubility of Sodium Phosphite in Water.

L. Amat prepared **lithium dihydrophosphite,** $LiH(HPO_3)$, by neutralizing phosphorous acid with lithium carbonate or hydroxide, using methyl orange as indicator, and evaporating to a syrup. The syrupy liquid is crystallized by allowing it to stand in vacuo. The salt is very soluble in water. L. Amat prepared **sodium dihydrophosphite,** $NaH(HPO_3).2\frac{1}{2}H_2O$, by neutralizing a soln. of phosphorous acid with sodium hydroxide or carbonate, and seeding the conc. soln. with a crystal of the salt previously prepared. The soln. is very prone to undercooling. A. Italiener obtained the soln. in a similar manner, and said that the syrupy liquid must stand in an ice-chest over phosphorus pentoxide for some time to crystallize.

L. Amat said that crystallization occurs when the aq. soln. is cooled to —23° ; and he obtained a soln. of the salt by the action of phosphorus trichloride on soda-lye—but the yield was poor. The salt loses all its water of crystallization in vacuo, or over conc. sulphuric acid ; while A. Italiener said that it is the anhydrous salt itself which crystallizes from the aq. soln. H. Dufet found that the salt prepared by L. Amat occurs in monoclinic prisms, with the axial ratios $a : b : c = 1{\cdot}2017 : 1 : 0{\cdot}7964$, and $\beta = 109° 53'$. The optical axial angle $2V = 77° 46'$ for Na-light, $77° 36\frac{1}{2}'$ for Li-light, and $77° 40'$ for Tl-light. The indices of refraction are $\alpha = 1{\cdot}4193$, $\beta = 1{\cdot}4309$, and $\gamma = 1{\cdot}4493$ for Na-light, while β for Li-light is 1·4281, and for Tl-light, 1·4334. The birefringence is positive. L. Amat gave 42° for the m.p. F. M. Raoult gave 0·307° for the lowering of the f.p. when one gram of the anhydrous salt is dissolved in 100 grms. of water ; and the mol. lowering of the f.p. is therefore 32·0. L. Amat gave for the heat of formation at 15°, $H_3PO_3 + NaOH = NaH_2PO_3 + H_2O_{solid} + 25{\cdot}2$ Cals. ; for the heat of hydration, $NaH_2PO_{3solid} + 2{\cdot}5H_2O_{solid} = NaH_2PO_3.2\frac{1}{2}H_2O. + 9{\cdot}65$ Cals. L. Amat gave for the heat of soln. of the anhydrous salt, 0·75 Cal. at 13°, and of the hemipentahydrate, —5·3 at 15°. J. Thomsen's observations on the heat of neutralization of phosphorous acid have been previously discussed. A. Italiener, and I. Müller gave $6{\cdot}887 \times 10^{-5}$ for the hydrogen-ion conc. A. Italiener found the tendency of the salt to form undercooled soln. so great that it was difficult to measure the solubility ; L. Amat found 100 grms. of water at 0° dissolved 56 grms. of salt ; 66 grms. at 10° ; and 193 grms. at the m.p. L. Amat obtained **potassium dihydrophosphite,** $KH(HPO_3)$, by a process like that used for the sodium salt. The crystals retain some adsorbed water which is lost in vacuo at 100°. H. Dufet found that the crystals are monoclinic prisms with the axial ratios $a : b : c = 1{\cdot}3913 : 1 : 1{\cdot}7197$, and $\beta = 101° 49\frac{1}{2}'$. The optical axial angle $2V = 36° 14'$; and the index of refraction $\beta = 1{\cdot}45$. L. Amat found that 100 grms. of water at 10° dissolve 172 grms. of the salt.

C. A. Wurtz reported **sodium heptahydrotriphosphite,** $Na_2HPO_3.2H_3PO_3.\frac{1}{2}H_2O$, or $Na_2H_4(HPO_3)_3.\frac{1}{2}H_2O$, in prismatic crystals, by evaporating in vacuo a soln. of phosphorous acid one-third neutralized with sodium hydroxide. The salt is deliquescent in moist air ; it loses its water of crystallization at 200° ; and at 245°, the evolution of phosphine begins. C. A. Wurtz obtained **potassium heptahydrotriphosphite,** $K_2H_4(HPO_3)_3$, or $K_2HPO_3.2H_3PO_3$, by evaporating in vacuo the soln. obtained by one-third neutralizing phosphorous acid. The crystals melt without appreciable loss at 200°, but at 250°, begin to emit phosphine.

H. Rose noted that when ammonium phosphite is added to a soln. of cupric chloride, the flocculent precipitate is not decomposed by washing. C. A. Wurtz obtained a granular, crystalline precipitate of **copper phosphite,** $Cu(HPO_3).2H_2O$, by treating a soln. of cupric acetate with phosphorous acid ; and L. Amat evaporated in vacuo a soln. of copper carbonate in phosphorous acid, and obtained a gum-like or a crystalline mass. The blue crystals lose 25 per cent. of water when kept over sulphuric acid ; and they are partially decomposed at 120°. C. F. Rammelsberg said the salt can be boiled in water without decomposition, but, according to H. Rose, the salt is reduced by boiling with phosphoric acid ; and L. Amat was unable to prepare the acid-salt because of this reduction. H. Rose found that when heated in a retort much water and hydrogen, but not phosphine, are given off, and a mixture of copper and normal copper phosphate remains. R. Kremann showed that when a soln. of sodium phosphite containing some copper salt is electrolyzed, some copper migrates to the anode, and he therefore assumes that a *hydrophosphitocupric acid* is present in the soln. $H(CuPO_3)$, or rather a *sodium cupric phosphite*, $Na[CuPO_3]$. A. Rosenheim and co-workers could not prepare complex cupric phosphites. In spite of the reducing action of phosphites on silver salts—*vide supra*—A. Sänger was able to make **silver phosphite,** Ag_2HPO_3, as a white crystalline precipitate, by adding silver nitrate to a soln. of phosphorous acid. The salt quickly turns brown, and ultimately forms a black powder. No *gold phosphite* has been reported.

H. Rose obtained a white precipitate of **calcium phosphite,** $CaHPO_3.2H_2O$, by mixing soln. of ammonium phosphite and calcium chloride ; and C. A. Wurtz, by neutralizing a soln. of phosphorous acid with ammonia, and then adding calcium chloride—rejecting the first fraction precipitated. C. F. Rammelsberg obtained calcium phosphite by mixing an aq. soln. of phosphorus trichloride with calcium chloride, and adding ammonia. P. L. Dulong found that the salt crystallizes by the slow evaporation of its aq. soln. C. A. Wurtz found that the water of crystallization is lost at 205° ; and C. F. Rammelsberg, at 200°–300°. At a red-heat hydrogen is given off, and calcium pyrophosphate is formed along with some phosphorus which colours the residue yellowish-brown. R. Rother said that when heated in a tube, phosphine is given off with a feeble detonation, and that at a certain temp., the mass suddenly becomes incandescent. P. L. Dulong found that the salt is hydrolyzed by boiling water with the precipitation of a basic phosphite, and the dissolution of an acid salt. H. Rose, and C. F. Rammelsberg prepared **strontium phosphite,** $Sr(HPO_3).1\frac{1}{2}H_2O$, by methods analogous to those employed for the calcium salt. P. L. Dulong said that the salt is sparingly soluble in water, and the soln. crystallizes when allowed to evaporate spontaneously. P. L. Dulong obtained crystals by the slow evaporation of its aq. soln. The crystalline precipitate was found by C. F. Rammelsberg to lose its water of crystallization at 200°–250°, and the loss of the last mol of water is attended by a partial decomposition of the salt whereby hydrogen and a little phosphine is given off. The residue contains strontium pyrophosphate mixed with a little red phosphorus. P. L. Dulong found that the salt is hydrolyzed in a boiling aq. soln., forming an insoluble basic salt, and a soluble acid salt.

J. J. Berzelius made normal **barium phosphite,** $BaHPO_3$, by mixing soln. of ammonium phosphite and barium chloride ; after the soln. has been allowed to stand for some time, a white crystalline crust of the phosphite appears on the liquid. C. F. Rammelsberg obtained the solid salt as a precipitate by adding ammonia to a soln. of the acid phosphite. A. Italiener prepared an aq. soln. of the salt by mixing soln. of sodium phosphite and barium chloride. The conditions of equilibrium in the presence of soln. of phosphorous acid are indicated in Fig. 36. P. L. Dulong found that an aq. soln. of the salt yields crystals on evaporation. The salt was analyzed by J. J. Berzelius, H. Rose, C. Zimmermann, and C. A. Wurtz, who reported the salt to be anhydrous $BaHPO_3$; but, according to A. Italiener, the salt is hemihydrated, $BaHPO_3.\frac{1}{2}H_2O$. C. F. Rammelsberg observed very little loss in weight—1·71 per cent.—at 200°–250° ; but when heated to redness, C. F. Rammelsberg, in agreement with H. Rose, observed that hydrogen and water are given off while the pyrophosphate, accompanied by a little phosphorus, remains. When the salt is evaporated with nitric acid, J. J. Berzelius found that the pyrophosphate is produced, while C. F. Rammelsberg obtained barium metaphosphate and nitrate as well. P. L. Dulong found that the salt is only sparingly soluble in water. A. Italiener showed that 100 grms. of soln. contained 0·6270 grm. of $BaHPO_3$ at 30°, and the result at 65° was very little different. P. L. Dulong observed that the salt is hydrolyzed by boiling water, forming an insoluble basic salt, and a soluble acid salt. H. W. F. Wackenroder found that barium phosphite is soluble in an aq. soln. of ammonium chloride.

Three acidic salts of barium phosphite have been reported with $BaHPO_3 : H_3PO_3$ as 2 : 1, 1 : 1, and 2 : 3. A. Italiener examined the ternary system $BaO–P_2O_3–H_2O$ at 30°. The following is a selection from the results, where the numerical data refer to the number of grams of the given component present in 100 grms. of soln. :

BaO .	4·22	4·70	4·76	9·90	26·91	27·77	8·42	25·77
P_2O_4 .	1·41	3·38	3·70	4·17	9·22	9·26	18·56	36·34
	$BaHPO_3.\frac{1}{2}H_2O$		$Ba_2(H_2PO_3)_3 5H_2O$			$Ba(H_2PO_3)_2$		H_3PO_3

The results are plotted in Fig. 36. C. F. Rammelsberg reported **barium dihydrotriphosphite,** $2BaHPO_3.H_3PO_3.8H_2O$, *i.e.* $Ba_2H_2(HPO_3)_3.8H_2O$, to crystallize from a soln. of the normal phosphite in warm phosphorous acid. This appears to be the salt represented by A. Italiener as a pentahydrate. The conditions of equilibrium are indicated in Fig. 36; similar remarks apply to **barium dihydrodiphosphite,** $BaH_2(HPO_3)$. H. Rose said that the *hemihydrate* is formed when the normal phosphite is digested with not too large an excess of phosphorous acid, and evaporating the filtrate in vacuo. It intumesces when heated, and gives off a mixture of phosphine and hydrogen, and, according to C. F. Rammelsberg, leaves behind a mixture of the metaphosphate and pyrophosphate. C. A. Wurtz reported the *monohydrate* to be formed from a soln. of the normal phosphite in sulphuric acid, or of barium hydroxide in phosphorous acid. C. F. Rammelsberg by a similar process alleged that the *dihydrate* is formed; and L. Amat, the *trihydrate.* A. Italiener did not find one of these four hydrates in her study of the ternary system, Fig. 36; and a similar remark applies to C. F. Rammelsberg's **barium hexahydropentaphosphite,** $2BaHPO_3.3H_3PO_3.2H_2O$, or $Ba_2H_6(HPO_3)_5.2H_2O$, said to be obtained in acicular crystals by spontaneously evaporating a soln. of the normal phosphite in the calculated quantity of phosphorous acid.

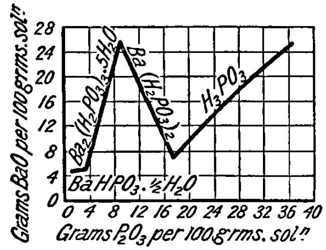

FIG. 36.—Solid Phases in the Ternary System: $BaO–P_2O_3–H_2O$.

H. Rose obtained **beryllium phosphite** as a white precipitate from soln. of ammonium phosphite and beryllium chloride. When heated in a retort, it becomes incandescent, giving off hydrogen but no phosphine. B. Bleyer and B. Müller could obtain only the feebly basic salt **beryllium oxytetraphosphite,** $4BeHPO_3.BeO.7H_2O$, as a white amorphous powder, from soln. of ammonium phosphite and beryllium sulphate. When heated, self-accendible phosphine is evolved, and beryllium pyrophosphate remains. H. Rose also made **magnesium phosphite,** $MgHPO_3.6H_2O$, by evaporating in vacuo the filtrate from a boiling soln. of magnesia is very dil. phosphorous acid. C. F. Rammelsberg obtained it from a soln. of magnesium carbonate in phosphorous acid; and the hemipentahydrate from a soln. of phosphorus trichloride and magnesium sulphate. The formula just indicated is based on the analysis of C. F. Rammelsberg. H. Rose found that at a red-heat much water is evolved, and then a mixture of hydrogen and phosphine, leaving a residue of the pyrophosphate coloured with red phosphorus. C. F. Rammelsberg added that the residue also contains some magnesia. When digested with nitric acid, magnesium pyrophosphate is formed. H. Rose said that the salt is sparingly soluble in water, and more soluble in cold than in hot water. L. Amat prepared the acidic salt, **magnesium dihydrodiphosphate,** $MgH_2(HPO_3)_2$, analogous to the corresponding salts of the three alkaline earths. H. Rose prepared **zinc phosphite,** $ZnHPO_3.2\frac{1}{2}H_2O$, by treating an aq. soln. of phosphorus trichloride, neutralized with ammonia, with zinc sulphate; part of the salt separates in the cold, and part on boiling, since the salt is more soluble in cold than it is in hot water. By treating an alkali phosphite soln. with zinc sulphate, A. Rosenheim, S. Frommer and W. Händler obtained the salt $3ZnHPO_3.8H_2O$. C. F. Rammelsberg used a modification of H. Rose's process and found that the salt loses its water of crystallization at 280°, and at a red-heat gives off hydrogen and only a trace, if any, of phosphine. There remains a mixture of zinc phosphide and pyrophosphate. If the aq. soln. be evaporated spontaneously in air, it furnishes the anhydrous phosphite. C. F. Rammelsberg evaporated soln. of the normal phosphite in phosphorous acid of different conc. and obtained acidic salts, **zinc hydrophosphites,** represented by $Zn_2H_3P_3O_8.2H_2O$; $Zn_3H_5P_5O_{13}.3H_2O$; and $Zn_2H_9P_5O_{14}.H_2O$. Neither the conditions of equilibrium nor the individuality of these products has been established. C. F. Rammelsberg obtained **cadmium phosphite,** $CdHPO_3$, as a white powder, from mixed soln. of cadmium sulphate and sodium or ammonium phosphite. A. Rosenheim, S. Frommer and W. Händler treated a soln. of cadmium sulphate with alkali phosphite, and obtained the salt, $3CdHPO_3.5H_2O$; they could not make complex cadmium phosphites. According to C. F. Rammelsberg, when the phosphite is heated, hydrogen almost free from phosphine is given off, some cadmium sublimes, and there remains a mixture of cadmium and its phosphide and pyrophosphate. H. Rose obtained **mercuric phosphite** as a white powder on adding phosphorous acid to a soln. of mercuric nitrate; the product decomposes with the separation of mercury as soon as it is warmed.

H. Rose neutralized an aq. soln. of phosphorus trichloride with ammonia, and added a soln. of alum in excess, when **aluminium phosphite** was formed as a white powder which gave off a mixture of hydrogen and phosphine when heated to redness. B. Grützner obtained **aluminium hydroxyphosphite,** $2Al(OH)_3.Al_2(HPO_3)_3$, by adding phosphorous acid to a slurry of colloidal alumina and water. If the clear soln. is boiled, a precipitate is obtained which when heated gives off phosphine. The analysis corresponds with the formula just indicated. L. Amat obtained well-defined crystals of **thallous hydrophosphite,** $TlH(HPO_3)$, by neutralizing a soln. of phosphorous acid with thallous carbonate. The salt melts at 70°–71°, and is very soluble in water. In summer it attracts moisture from the atm., and becomes liquid; in winter, it becomes solid again. It is neutral towards methyl-orange.

H. Rose neutralized an aq. soln. of phosphorus trichloride, with ammonia, and added an aq. soln. of titanium tetrachloride, the resulting white precipitate contained some **titanium phosphite.** When heated, it gave a mixture of hydrogen and phosphine; and left a black residue of reduced titanic oxide—not the monoxide. O. Kauffmann added phosphorous acid to a soln. of thorium nitrate, and warmed the mixture on a water-bath. The white product was **thorium phosphite,** $Th(HPO_3)_2.3H_2O$. It gradually oxidized at 105°; it was insoluble in water and in dil. acids and alkali-lye; but dissolved slowly in mineral acids, particularly when warmed. If soln. of sodium hydrophosphite and thorium nitrate be mixed as before, the octohydrate, $Th(HPO_3)_2.8H_2O$, is formed.

H. Rose obtained **stannous phosphite,** $Sn(HPO_3)$, by treating a soln. of stannous chloride with ammonium phosphite and washing the white precipitate until the wash-water, boiled with nitric acid, gives no precipitate with silver nitrate. The salt blackens when heated, gives off hydrogen and phosphine, and a sublimate of phosphorus. It is gelatinized by heating with nitric acid, forming stannic phosphate. The soln. of the salt reduces many other metal salts. A. Rosenheim and co-workers obtained a similar product; but they could not obtain complex salts. H. Rose also obtained a white precipitate—possibly **stannic phosphite**—by the action of ammonium phosphite on stannic chloride. It develops water when heated, and the stannic oxide passes into stannous oxide. Normal **lead phosphite,** $Pb(HPO_3)$, was made by H. Rose, and J. J. Berzelius, by treating a soln. of lead acetate with ammonium phosphite; by L. Amat using lead nitrate and phosphorous acid or one of the sodium phosphites, or lead oxide and phosphorous acid, or by treating lead acid phosphite, pyrophosphite, or nitratophosphite with water; and by C. F. Rammelsberg, by neutralizing phosphorous acid with lead carbonate. The product retains about 2·7 per cent. of water. A. Rosenheim and co-workers obtained a similar product. According to H. Rose, and C. F. Rammelsberg, when lead phosphite is heated it develops hydrogen and phosphine, along with a sublimate of phosphorus, and leaves a residue of lead phosphide and pyrophosphate. According to V. Ipatieff, lead phosphite is converted into lead and phosphoric acid when heated in hydrogen. J. J. Berzelius said that the phosphite can be dissolved in cold nitric acid without decomposition, but when heated it forms the pyrophosphate. R. Weinland and F. Paul prepared **lead tetrabromophosphite,** $2PbBr_2.PbHPO_3.H_2O$; and **lead dichlorophosphite,** $PbCl_2.PbHPO_3.H_2O$. L. Amat prepared **lead dinitrato-phosphite,** $Pb_2(NO_3)_2(HPO_3)$, by adding an excess of lead nitrate to a cold soln. of sodium hydrophosphite; or sodium pyrophosphite; or by treating normal lead phosphite with a soln. of lead acetate in dil. nitric acid; or by treating lead phosphite with dil. nitric acid. The salt is stable in air, and at temp. up to 110°. If strongly heated, it explodes. Water decomposes it into lead nitrate and phosphite—

particularly if the water is boiling. If it is heated with nitric acid and calcined it forms a mixture of lead oxide and phosphate. C. A. Wurtz found that lead phosphite is reduced by warm sulphuric acid to sulphur dioxide; and H. Rose, that it is soluble in phosphorous acid, and the soln., according to C. A. Wurtz, gives white flocks with ammonia. When the normal phosphite is digested for some weeks with aq. ammonia, and the product washed with alcohol, H. Rose found that **lead dioxydiphosphite,** $4PbO.P_2O_3.2H_2O$, or $2PbO.2Pb(HPO_3).H_2O$, is formed; and C. A. Wurtz reported **lead oxydiphosphite,** $PbO.2Pb(HPO_3)$. L. Amat found that the soln. of the normal phosphite in phosphorous acid yields **lead dihydrodiphosphite,** $PbH_2(HPO_3)_2$, which can be washed with absolute ether and dried in vacuo or at 100°. The colourless crystals form the pyrophosphite at 100°; water forms normal lead phosphite and phosphorous acid. A. Rosenheim and co-workers could not prepare complex salts.

H. Rose prepared **antimonyl phosphite,** $(SbO)H_2PO_3$, by neutralizing an aq. soln. of phosphorus trichloride with ammonia, and adding tartar emetic; the white precipitate gives off hydrogen when heated, and it is soluble in hydrochloric acid. B. Grützner treated antimony oxide with a soln. of phosphorous acid, and obtained microscopic needles of the above composition. No salt could be prepared from antimony oxide, and potassium hydrophosphite. B. Grützner also prepared **bismuth phosphite,** $Bi_2(HPO_3)_3.3H_2O$, by the action of phosphorous acid on bismuth oxide; and L. Vanino and F. Hartl, by adding phosphorous acid to a soln. of bismuth nitrate and mannite. H. Rose obtained the salt by neutralizing an aq. soln. of phosphorus trichloride with ammonia, and adding a soln. of bismuth chloride as nearly neutral as possible. The small, four-sided, acicular crystals are almost insoluble in water; they lose their water of crystallization at 105°; and when heated give off hydrogen alone. L. Vanino and F. Hartl said the salt is not decomposed by potash-lye; it reacts slowly with potassium iodide; and rapidly with hydrogen sulphide.

H. Rose treated an aq. soln. of chromic chloride with a soln. of phosphorus trichloride, and obtained **chromium phosphite,** partly as a green soln., and partly as a precipitate. The phosphite appears as a voluminous, green powder, which when heated gives off hydrogen but no phosphine. A. Rosenheim and S. Frommer prepared a series of salts, $R[Cr(HPO_3)_2].nH_2O$, by the action of a conc. soln. of chromium chloride on an aq. soln. of an alkali phosphite, *e.g.* **ammonium chromium phosphite,** $NH_4[Cr(HPO_3)_2].8H_2O$; **potassium chromium phosphite,** $K[Cr(HPO_3)_2].12H_2O$; **sodium chromium phosphite,** $Na[Cr(HPO_3)_2].14H_2O$, as well as a guanidinium salt. A. Italiener also reported complex $K[Cr(HPO_3)_2].12H_2O$; and $K_8[Cr_6(HPO_3)_{13}].52H_2O$, to be formed by mixing soln. of chromic chloride and potassium phosphite; likewise with sodium chromium phosphite, $Na_4[Cr(HPO_3)_2].14H_2O$; $Na[Cr(HPO_3)_2.Na_2HPO_4.73H_2O$; $Na_4[Cr_2(HPO_3)_5].39H_2O$; and ammonium chromium phosphite. A guanidine salt was also prepared. O. W. Gibbs prepared **ammonium phosphitohexamolybdate,** $(NH_4)_2O.6MoO_3.H_3PO_3.6H_2O$, by the action of soln. of ammonium molybdate on phosphorous acid. A. Rosenheim and M. Schapiro prepared a series of heteropolymolybdates with the general formula $2R_2O.P_2O_3.12MoO_3.nH_2O$, and also $2R_2O.P_2O_3.5MoO_3.nH_2O$. The former by dissolving phosphorous acid in an excess of alkali molybdate (say 1 : 6) acidifying the soln. with hydrochloric acid, and warming the liquid; and the latter by adding 2 mols of molybdium trioxide to a boiling aq. soln. of a mol of alkali phosphite, and allowing the liquid to crystallize. They thus obtained **ammonium phosphitododecamolybdate,** $2(NH_4)_2O.P_2O_3.12MoO_3.23H_2O$, and **ammonium phosphitopentamolybdate,** $2(NH_4)_2O.P_2O_3.5MoO_3.7H_2O$; M. Weinberg also reported an ammonium phosphitohexamolybdate, $(NH_4)_3[P(Mo_2O_7)_3].6H_2O$; M. Weinberg reported a **potassium phosphitohexamolybdate,** $K_2[P(Mo_2O_7)_3].11H_2O$; and A. Rosenheim and M. Schapiro, $2K_2O.P_2O_3.12MoO_3.9H_2O$(and $17H_2O$), and **potassium phosphitopentamolybdate,** $2K_2O.P_2O_3.5MoO_3.6H_2O$. They also obtained **lithium phosphitododecamolybdate,** $2Li_2O.P_2O_3.12MoO_3.19H_2O$; and

sodium phosphitododecamolybdate, $2Na_2O.P_2O_3.12MoO_3.19H_2O$(and $41H_2O$). W. Weinberg also prepared the salt $Na_3[P(Mo_2O_7)_3].10H_2O$, as well as a *guanidine salt*. O. W. Gibbs also reported **ammonium phosphitotungstate,** $6(NH_4)_2O.22WO_3.4H_3PO_3.25H_2O$; **potassium phosphitotungstate,** $5K_2O.32WO_3.16H_3PO_3.46H_2O$, as well as $5K_2O.24WO_3.2H_3PO_3.13H_2O$; and **sodium phosphitotungstate,** $2Na_2O.22WO_3.8H_3PO_3.35H_2O$; and W. Weinberg, **sodium phosphitohexatungstate,** $Na_3[P(W_2O_7)_3].16H_2O$. O. W. Gibbs reported ill-defined **copper phosphitotungstates,** and **mercurous phosphitotungstates.** A. Rodgers boiled for 5 hrs. a mixture of 1·5 grms. of ammonium phosphite, one gram of vanadium trioxide, 20 grms. of ammonium tungstate, 23 c.c. of aq. ammonia, and 700 c.c. of water; evaporated the mixture to one-third its original vol.; and obtained black octahedra of **ammonium tetraphosphitotetradecavanaditohenitricontatungstate,** $14(NH_4)_2O.2P_2O_3.7V_2O_3.31WO_3.78H_2O$.

V. Kohlschütter and H. Rossi noted the possible existence of **uranous phosphite;** and C. F. Rammelsberg obtained **uranyl phosphite,** $(UO_2)_3H_2(HPO_3)_4.12H_2O$, by adding ammonium uranate to an aq. soln. of phosphorus trichloride. The yellow precipitate loses 9·03 per cent. of moisture when dried over conc. sulphuric acid; 10·52 per cent. at 180°; 11·79 per cent. at 240°; and 16·45 per cent. at 300°. The residue is green. A. Rosenheim and H. Gläser prepared a series of alkali uranyl phosphites by adding a soln. of uranyl or sulphate drop by drop to a conc. soln. of alkali phosphite until the precipitate no longer dissolves when the mixture is vigorously shaken. The liquid on standing deposits deep yellow crystals. They thus obtained **potassium uranyl phosphite,** $K_2[UO_2(HPO_3)_2]$; **ammonium uranyl phosphite,** $(NH_4)_2[UO_2(HPO_3)_2]$; and **sodium uranyl phosphite,** $Na_2[UO_2(HPO_3)_2]$. M. Lobanoff obtained **uranium phosphite,** $U(HPO_3)_2.4H_2O$; and **uranium hydrophosphite,** $U(HPO_3)(H_2PO_3)_2$, by adding the requisite proportion of the acid to acidic soln. of uranic sulphate.

H. Rose, and C. F. Rammelsberg reported **manganous phosphite,** $MnHPO_3.H_2O$, by neutralizing an aq. soln. of phosphorus trichloride with ammonia, and adding a manganous salt. The precipitate is reddish-white. C. F. Rammelsberg dissolved manganous carbonate in phosphorous acid, and neutralized the soln. with sodium carbonate. When heated to redness in a retort the salt often becomes incandescent, and develops hydrogen along with phosphine, and some red phosphorus sublimes; the residue is mainly pyrophosphate mixed with phosphide, or, as C. F. Rammelsberg represented the reaction: $7MnHPO_3=3Mn_2P_2O_7+MnP+7H$. H. Rose said the salt dissolves with difficulty in water, but it dissolves readily in soln. of manganous chloride and sulphate. L. Vanino found the salt reacts slowly with potassium sulphide. A. Rosenheim, S. Frommer and W. Händler obtained deep violet-red soln. by mixing salts of tervalent manganese with soln. of alkali phosphites, but owing to hydrolysis obtained only impure *sodium manganese phosphite*. H. Rose prepared a **ferrous phosphite** by neutralizing an aq. soln. of phosphorus trichloride, and adding ferrous sulphate. The precipitate is washed with boiling water and dried. It is a white powder which readily oxidizes and becomes green. When heated it gives off hydrogen and forms ferrous pyrophosphate; the reaction may be accompanied by incandescence. J. A. Krenner described a reddish-brown ferrous phosphite, $nFeO.P_2O_3$, occurring as a mineral, which he named *schafarzikite*—after F. Schafarzik. The crystals are tetragonal pyramids with the axial ratio $a:c=1:9787$. L. Tokody gave 1 : 0·95381. The crystals are isomorphous with trippkeite. According to L. Tokody, the pleochroic crystals have ω straw-yellow, and ϵ brownish-yellow. The index of refraction is 1·740, the birefringence is feeble, and the optical character is positive. The sp. gr. is 4·3; and the hardness, 3·5. A. Rosenheim and co-workers could not prepare complex ferrous phosphites. B. Grützner obtained a soln. of **ferric phosphite** by dissolving ferric oxide in phosphorous acid. The precipitate obtained by adding water has a variable composition, but E. Berger showed that if the precipitate be thoroughly washed with cold water to remove all the phosphorous acid, the white powder has a constant composition, that of **ferric**

trihydroxyhexaphosphite, $2Fe_2(HPO_3)_3.Fe(OH)_3.5H_2O$. If, in the preparation of ferrous phosphite, the ferrous sulphate is replaced by ferric chloride or ammonium ferric sulphate, the white precipitate of ferric phosphite, $Fe_2(HPO_4)_3.9H_2O$, is soluble in an excess of the soln. of the ferric salt. If ammonia be in excess, a basic ferric phosphite may be formed. When the ferric salt is heated, H. Rose said that hydrogen and phosphine are given off, but C. F. Rammelsberg found only hydrogen, and a residual mixture of ferric pyrophosphate, and ferrous phosphate. A. Rosenheim, S. Frommer and W. Händler added a cold, conc. soln. of ferric chloride to a sat. soln. of ammonium or alkali phosphite, and obtained **sodium ferric hydroxyphosphite,** $Na_2[Fe(OH)(HPO_3)_2].20H_2O$; **potassium ferric hydroxyphosphite,** $K_2[Fe(OH)(HPO_3)_2].20H_2O$; and **ammonium ferric hydroxyphosphite,** $(NH_4)_2[Fe(OH)(HPO_3)_2].8H_2O$.

H. Rose obtained a red precipitate of **cobalt phosphite,** $CoHPO_3.2H_2O$, by treating a soln. of ammonium phosphite with cobalt chloride; and C. F. Rammelsberg, by treating cobalt carbonate with an aq. soln. of phosphorus trichloride. The dried salt is pale red, but after drying at 250°, is blue. It loses its water of crystallization at 250°. When calcined in a retort, the mass may become incandescent. C. F. Rammelsberg represented the reaction: $7CoHPO_3=3Co_2P_2O_7+CoP+7H$; and when evaporated with nitric acid, it yields the pyrophosphate. As in the case of the cupric salt, R. Kremann assumed the existence of *sodium cobaltophosphite*, $NaCoPO_3$. A. Rosenheim, S. Frommer and W. Händler treated a salt of bivalent cobalt with ammonium or potassium phosphite and obtained **ammonium cobalt phosphite,** $(NH_4)_2[Co_3(HPO_3)_4].18H_2O$; and **potassium cobalt phosphite,** $K_2[Co_3(HPO_3)_4].32H_2O$. H. Rose, and C. F. Rammelsberg prepared **nickel phosphite,** $NiHPO_3.H_2O$, by the methods employed for cobalt phosphite. According to H. Rose, nickel phosphite loses all its water at 250°; and when heated in a retort it gives off hydrogen alone, and, according to C. F. Rammelsberg, the residue is a mixture of the pyrophosphate with a trace of phosphide. When evaporated with nitric acid, nickel pyrophosphate is formed. R. Kremann assumed the existence of *sodium nickelophosphite*, $Na[NiPO_3]$. A. Rosenheim, S. Frommer and W. Händler treated a salt of bivalent nickel with an alkali or ammonium phosphite, and obtained **ammonium nickel phosphite,** $(NH_4)_2[Ni_3(HPO_3)_4].18H_2O$; and **potassium nickel phosphite,** $K_2[Ni_3(HPO_3)_4].32H_2O$.

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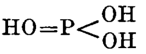
§ 19. Metaphosphorous and Pyrophosphorous Acids and their Salts

According to H. J. van de Stadt,[1] if oxygen and phosphine, both thoroughly dried, be mixed slowly, a greenish-blue, often intermittent, combustion occurs and **metaphosphorous acid,** HPO_2, is formed: $PH_3+O_2=H_2+HPO_2$; and if the press. of the gases is low, crystals of the acid collect on the walls of the containing vessel. The crystals do not melt at 80°, and they react with water, forming phosphorous acid: $HPO_2+H_2O=H_3PO_3$.

It will be observed that ordinary phosphorous acid may be regarded as orthophosphorous acid, $P(OH)_3$, which has undergone some intramolecular change, forming $H-PO=(OH)_2$; if the meta-acid is regarded as a derivative of the ortho-acid by the loss of water, then the condensation of two mols of the ortho-acid, with the loss of water, will furnish normal **pyrophosphorous acid,** $H_4P_2O_5$:

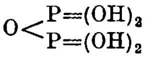
$HO-P=O$

Metaphosphorous acid, HPO_2.



$HO=P<\genfrac{}{}{0pt}{}{OH}{OH}$

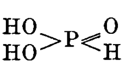
Orthophosphorous acid, H_3PO_3.



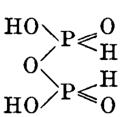
$O<\genfrac{}{}{0pt}{}{P=(OH)_2}{P=(OH)_2}$

Pyrophosphorous acid, $H_4P_2O_5$.

Owing to the peculiar intramolecular change which attends the conversion of orthophosphorous acid into ordinary phosphorous acid, it is probable that the normal pyrophosphorous suffers a similar change whereby the phosphorus passes to the quinquevalent form:



Phosphorous acid.



Pyrophosphorous acid.

In 1864, N. Menschutkin first obtained a derivative of pyrophosphorous acid in the form of acetopyrophosphorous acid, $H_3(C_2H_3O)P_2O_5$. In 1888, L. Amat showed that the secondary phosphites lose water when heated, forming pyrophosphites; which can be regarded as derivatives of a special pyrophosphorous acid, so that H_3PO_3 is related to $H_4P_2O_5$, the same as H_3PO_4 is related to $H_4P_2O_7$. He obtained a soln. of the very unstable pyrophosphorous acid by treating at as low a temp. as practicable a dil. soln. of barium pyrophosphite with an eq. amount of dil. sulphuric acid. He estimated the heat of decomposition to be $H_4P_2O_{5aq.}=2H_3PO_{3aq.}+4{\cdot}9$ Cals.; and the heat of neutralization: $H_4P_2O_{5aq.}+2NaOH_{aq.}=Na_2H_2P_2O_{5aq.}+2H_2O+28{\cdot}6$ Cals. L. Amat made about half a dozen pyrophosphites. In aq. soln., they readily form hydrophosphites: $Na_2H_2P_2O_5+H_2O=2POH(ONa)(OH)$, and this the more rapidly, the greater the conc. of the soln., and the higher the temp. Increasing the acidity of the soln.—by, say, sulphuric acid—also accelerates the reaction. The thermal properties of the pyrophosphites are said by L. Amat to prove that they are not ordinary hydrophosphites.

L. Amat prepared **sodium dihydropyrophosphite**, $Na_2H_2P_2O_5$, in vacuo at about 160° until it has lost its water. The product is freely soluble in water, and the aq. soln. is unlike one of sodium hydrophosphite in that it is neutral to both methyl-orange and phenolphthalein. The soln. is stable when cold, but when boiled, it is converted into the hydrophosphite; it is the more stable, the less its conc., but a conc. soln. can be evaporated for crystallization. The presence of acids lessen the stability of the soln. The rate of conversion follows the mass law. The change is more rapid the more conc. the soln., but the effect of dilution becomes smaller and smaller as the conc. diminishes. With soln. so dil. that the concentration is without influence, the rate of change is proportional to the quantity of acid present. Nitric and hydrochloric acids exert the greatest effect, sulphuric acid somewhat less, and phosphorous acid still less, whilst acetic acid has only a very slight effect. The change in presence of alkali is subject to similar laws, the rate of change at each instant being proportional not only to the quantity of pyrophosphite present in the soln. but also to the quantity of free alkali. The heat of hydrolysis: $Na_2H_2P_2O_{5solid}+H_2O_{solid}=2NaH(HPO_3)_{solid}+6{\cdot}24$ Cals.; and the heat of soln. at 13° is 0·3 Cal. The corresponding **potassium dihydropyrophosphite** was made in a similar way. White **calcium dihydropyrophosphite**, $CaH_2P_2O_5$, was made by heating the monohydrated hydrophosphite for 2 days at 150°. The salt is not completely soluble in water, but is freely soluble in hydrochloric acid. The soln. with both solvents smell of phosphine. The analogous **strontium dihydropyrophosphite**, $SrH_2P_2O_5$, and likewise **barium dihydropyrophosphite**, $BaH_2C_2O_5$, were prepared by heating the monohydrated hydrophosphite for 150 hrs. at 120°–150°. L. Amat also made **thallium dihydrophosphite**, $Tl_2H_2P_2O_5$, and **lead dihydropyrophosphite**, $Pb_2H_2P_2O_5$, in a similar way. When a soln. of sodium dihydropyrophosphite is treated with lead nitrate, the lead nitratophosphite is formed. The lead salt is readily hydrolyzed by water.

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§ 20. Phosphorus Tetroxide or Phosphorosic Oxide

According to T. E. Thorpe and A. E. H. Tutton,[1] when phosphorus glows in air at ordinary temp., phosphoric oxide is the only oxide of phosphorus formed; at higher temp.—about 50°–60°—phosphorous oxide begins to appear, but only when the phosphorus is ignited does any considerable proportion of that oxide appear. This is in agreement with the observations of R. Cowper and V. B. Lewes,

N. Blondlot, indeed, believed that phosphoric oxide is always the primary product, and that the phosphorous oxide is the result of a secondary reaction: $3P_2O_5+4P=5P_2O_3$. M. Pagels said that the proportion of phosphorous to phosphoric oxide rarely exceeds 1:3, but T .E. Thorpe and A. E. H. Tutton obtained a ratio nearly 1:1. In addition to these oxides, when phosphorus burns at a moderately high temp. in a limited supply of air, phosphorus tetritoxide is formed (*q.v.*). P. Hautefeuille and A. Perrey obtained a crystalline sublimate by heating the products of the combustion of phosphorus, but they regarded it as an allotropic form of phosphoric oxide. T. E. Thorpe and A. E. H. Tutton showed that the sublimate was more probably a specific oxide. According to T. E. Thorpe and A. E. H. Tutton, if the mixed oxides formed by the slow burning of phosphorus in air dried by phosphorus pentoxide be heated in an evacuated sealed tube at about 290°, the white mass becomes orange or red, and a sublimate of transparent, lustrous crystals is formed. C. A. West employed a somewhat similar mode of preparation. V. Kohlschütter and A. Frumkin observed that some tetroxide is formed by the decomposition of the red deposit produced when phosphorus oxidizes in oxygen at a low press.; E. J. Russell, when the white deposit formed by oxidizing phosphorus in oxygen at a high press. is heated in vacuo; and C. C. Miller, when phosphorus trioxide oxidizes in moist oxygen at 25° and 600 mm. press.

The analysis of the oxide by T. E. Thorpe and A. E. H. Tutton, and C. A. West corresponds with the empirical formula PO_2. The former workers assumed that this oxide is analogous with nitrogen and antimony tetroxides. C. A. West found that the vap. density at a temp. exceeding 1400° was 229·3, hydrogen unity; hence the mol. wt. is 458·6, corresponding with the formula P_8O_{16}. This oxide does not therefore fall in line intermediate between phosphorous oxide, P_4O_6, and phosphoric oxide, P_4O_{10}. No suitable solvent is known to enable the cryoscopic and ebulliscopic methods to be applied. The term **phosphorus tetroxide** is therefore a misnomer, although it is usually retained because it has crept into the literature of the subject. Similar remarks apply to many other compounds—*e.g.* phosphorus trioxide and pentoxide, etc. It might also be called *phosphorosophosphoric oxide*, a term which can be abbreviated to **phosphorosic oxide.** According to T. E. Thorpe and A. E. H. Tutton, phosphorosic oxide cannot be regarded as the anhydride of hypophosphoric acid—*vide infra*—even though its composition has a formal resemblance to that of the unknown *hypophosphoric anhydride*, because hypophosphoric acid exerts no reducing action on the chlorides of mercury, gold, or silver, and forms a sparingly soluble sodium salt. The aq. soln. of phosphorosic oxide does not possess these properties. Phosphorosic oxide is not to be regarded as a mere compound of phosphorous and phosphoric oxides, and it is derived from phosphorous oxide either by the elimination of red phosphorus: $2P_4O_6=3P_2O_4+2P$, or of phosphorus tetritoxide: $7P_4O_6=2P_4O+10P_2O_4$.

Phosphorosic oxide forms white rhombic crystals which on a cursory glance seem to be cubical. The polarization phenomena do not agree with those of tetragonal crystals, and their holosymmetry is not in agreement with hexagonal crystals. The crystals were far too deliquescent in air to allow the crystallographic measurements to be made. C. A. West found the sp. gr. to be 2·537 at 22·6°/4°. Heat does not cause any appreciable change; the crystals sublime without melting and without decomposition. T. E. Thorpe and A. E. H. Tutton said that no visible change occurs at 100°, but sublimation proceeds at 180°. C. A. West found that a sample exposed for 12 months to daylight suffered no visible change. The general reactions of phosphorosic oxide in aq. soln. shows that it probably breaks down into phosphorous and metaphosphoric acids: $2PO_2+2H_2O=HPO_3+H_3PO_3$. Attempts to determine the relative proportions of the two acids did not yield concordant results.

The aq. soln. was found by T. E. Thorpe and A. E. H. Tutton to require repeated evaporation with *nitric acid* in order to oxidize the phosphorosic oxide to phosphoric acid. An aq. soln. of the oxide neutralized with *sodium hydroxide* behaves like a soln. of normal sodium phosphite. A boiling soln. of soda-lye does not affect phosphites, but decomposes hypophosphites into a phosphate with the elimination of hydrogen ; a soln. of phosphorosic oxide in water behaves towards *silver nitrate* like a soln. of the same oxide which has been boiled with soda-lye. In both cases, a white or yellow precipitate is formed which quickly turns brown and finally black. In aq. soln., *calcium chloride* gives no precipitate at first, but a flocculent white precipitate is obtained on adding ammonia ; *barium chloride or hydroxide* gives a white precipitate, soluble in hydrochloric acid, but not soluble in acetic acid. An ammoniacal soln. of *magnesium chloride—magnesia mixture*—gives no precipitate with phosphites and hypophosphites except in very conc. soln. ; with a soln. of phosphorosic oxide, there is an immediate precipitate of what C. A. West called magnesium metaphosphate, and T. E. Thorpe and A. E. H. Tutton, ammonium magnesium phosphate. A soln. of *mercuric chloride* gives a white precipitate which forms slowly hot or cold ; *lead nitrate* gives a white precipitate insoluble in acetic acid ; and a hot or cold soln. of *potassium permanganate* is slowly decolorized. According to C. A. West, *benzene, naphthalene, phenol, nitrobenzene, chloroform, carbon disulphide,* and *ether* seemed to be entirely without action on the oxide, whilst *acetone* was turned slightly brown and *acetic acid* became deep brown. This action seems to resemble that of the commercial phosphorus pentoxide on acetic acid.

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§ 21. Hypophosphoric Acid

In 1877, T. Salzer,[1] in his memoir : *Ueber die Unterphosphorsäure,* proved that B. Pelletier's *acide phosphatique* contained an acid previously unrecognized. It is now called **hypophosphoric acid,** $H_4P_2O_6$, or H_2PO_3 ; and sometimes *subphosphoric acid.* The phosphatic acid is prepared by the slow oxidation of phosphorus in air in the presence of water as indicated in connection with phosphorous acid. T. Salzer prepared the *acidum phosphori per deliquium* by placing sticks of phosphorus in glass cylinders half covered with water. The cylinders were suspended by a string in an earthenware mug loosely covered with a sheet of glass. Every third day the liquid in the cylinders was collected, and the sticks of phosphorus again half covered with water. He added that the oxidation of the phosphorus is much assisted, if large quantities are left to the action of the air and water in the same space. This is effected, probably not by rise of temp., but by the stronger ozonizing of the air, or otherwise by the more active formation of hydrogen peroxide, for the phosphorus is most corroded where it dips into the liquid. It is also remarked that the formation of the hypophosphoric acid proceeds with that of the phosphorous and phosphoric acids in a certain ratio, until the liquid becomes so conc. that no more of the first acid can be formed : only about 6 or 7 per cent. of the phosphorus is converted into hypophosphoric acid, phosphoric acid being the chief product. The hypophosphoric acid was separated in the form of a sparingly soluble sodium salt by treating the acid with the alkali carbonate or acetate. A. Joly found that the oxidation of the phosphorus in the preparation of phosphatic acid occupies 48 hrs. in summer, and longer in winter. In summer, 10 per cent. of the phosphorus is oxidized to this acid, and in winter 12–14 per cent. According to A. Rosenheim, W. Stadler, and F. Jacobsohn, the phosphorus is oxidized very slowly below 5°, and above 10°, the oxidation is so rapid that marked quantities of meta- and orthophosphoric acids are produced in consequence of local heating on the surface of the sticks of phosphorus. A. Joly obtained sodium hypophosphate by adding sodium carbonate to the boiling acid until neutral to methyl-orange ; when the liquid, conc. by evaporation, is cooled, the sodium salt separates. It is washed with cold water, and recrystallized from boiling water as $Na_2H_2P_2O_6.6H_2O$. T. Salzer said that the sodium salt can be prepared directly by exposing in air sticks of phosphorus partially immersed in a dil. soln. of sodium chloride (1 : 100). P. Drawe recommended T. Salzer's process for preparing *le acide phosphatique,* but he preferred collecting the oxidation products in a 25 per cent. soln. of sodium acetate in place of water. C. Bansa used a similar process. H. Schuh compared the different modes of preparing the acid.

J. Cavalier and E. Cornec's method of preparing hypophosphoric acid by the slow oxidation of phosphorus in the presence of water, is as follows: Glass rods are placed horizontally on a photographic dish : sticks of phosphorus are placed transversely over the rods, and glass rods are placed between the sticks of phosphorus to prevent their touching, and so possibly igniting. Water is poured into the dish until the sticks of phosphorus are half submerged. The dish is kept in a cool place, and covered with a glass plate with a roll of wadding as intermediary so that filtered air can slowly find its way into the dish. With a dish 13 × 18 cms., it is possible to get 30–50 grms. of the sodium salt in 5–6 days. The acid liquor is treated for the sodium salt as already described.

T. Salzer found that hypophosphoric acid is formed during the slow oxidation of phosphorous acid in air. Hypophosphoric acid is an intermediate product in the oxidation of phosphorus by cupric nitrate in the presence of dil. nitric acid, and J. Corne prepared hypophosphites by this process in 1882—ammonia, and phosphorous and phosphoric acids were by-products. P. Drawe adversely criticized this process. J. Philipp substituted silver nitrate for cupric nitrate. F. Tauchert observed that this acid is one of the products of the action of phosphorus on a soln. of copper sulphate. A. Sänger obtained the silver hypophosphate by oxidizing phosphorous acid with silver nitrate in neutral or ammoniacal soln. In this reaction, it is assumed that $8AgNO_3+2H_3PO_3+H_2O+8NH_3=Ag_4O+Ag_4P_2O_6+8NH_4NO_3$, and the silver oxide formed oxidizes the phosphorous acid to hypophosphoric acid. A. Rosenheim and J. Pinsker did not recommend this mode of preparation.

In A. Rosenheim and J. Pinsker's modification of J. Corne's process, 100 grms. of copper turnings are added to a mixture of 100 c.c. of water and 200 c.c. of nitric acid (sp. gr. 1·4) in a 3-litre flask. When the intensity of the reaction has subsided, yellow phosphorus is gradually added while the temp. is maintained between 50° and 70°. When the clear colourless liquid is decanted off, the copper is all precipitated as copper phosphide and spongy copper, and half is neutralized with sodium carbonate, and mixed with the other half. Crystals of the sodium salt, $Na_2H_2P_2O_6.4H_2O$, separate after a time. The yield with copper nitrate is 10 per cent. of the theoretical, but is not so good if silver nitrate is used in place of copper.

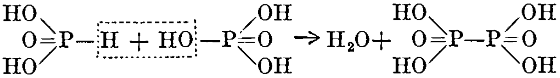
A. Rosenheim and J. Pinsker showed that zinc, manganese, nickel, cobalt, mercuric, and ferric nitrates do not give appreciable amounts of hypophosphoric acid—neither do the nitrogen oxides—if used in place of Corne's copper nitrate. A. Rosenheim and J. Pinsker consider that the formation of the acid is due to the action of the copper and not of the nitric acid since other salts of copper furnish hypophosphoric acid when treated with yellow phosphorus; according to F. Tauchert (1913), there are two reactions: $5Cu(NO_3)_2+4P+8H_2O=Cu_3P_2+2Cu+10HNO_3+2H_3PO_4$; and $4Cu(NO_3)_2+4P+6H_2O=H_4P_2O_6+Cu_3P_2+Cu+8HNO_3$—about 7 per cent. of the phosphorus is thus obtained as hypophosphoric acid, while as much as 20 per cent. may be effective with a hot soln. of copper sulphate. The nitric acid further reacts with the copper phosphide, forming phosphoric and phosphorous acids and nitric oxide. A. Rosenheim and J. Pinsker obtained as high as 60 per cent. yields of hypophosphoric acid by the electrolysis of 1–2 per cent. sulphuric acid soln. with copper, nickel, or silver phosphide as anode, and the corresponding metal as cathode. The phosphide is decomposed, and the phosphorus is oxidized to the acid. They used a current of 3–10 volts. With a cathode of iron phosphide, the oxidation was carried further and phosphoric acid alone was obtained.

T. Salzer isolated the acid by dissolving the sodium salt in hot water, and treating the soln. with lead acetate when an insoluble lead hypophosphate is precipitated. This salt is filtered from the soln. and washed with hot water. The precipitate is suspended in water, and a current of hydrogen sulphide passed through the soln. Lead sulphide is precipitated, and a soln. of free hypophosphoric acid is obtained. On evaporation, the excess of hydrogen sulphide is driven from the soln., but the evaporation cannot be carried very far without decomposing the acid. Hence, the soln. must be further evaporated in a desiccator in vacuo over sulphuric acid. This method is tedious, and not so good as when the barium salt is used in place of the lead salt. T. Salzer, A. Sänger, and A. Joly preferred to convert the sodium salt into the insoluble barium hypophosphite, which was then decomposed by treatment with an eq. amount of sulphuric acid. The filtered soln. was conc. in vacuo over sulphuric acid. In time crystals of the hydrate $H_2PO_3.H_2O$, or $H_4P_2O_6.2H_2O$, separate. A. Joly added that in preparing the acid, an elevation of temp., and an excess of sulphuric acid, should be avoided. The crystals of the hydrated acid are liable to decompose if left too long in contact with the mother-liquor.

Analyses by T. Salzer, A. Sänger, and A. Joly are in agreement with the empirical formula H_2PO_3. At first, T. Salzer considered the phosphorus hypophosphoric acid to be quadrivalent, and wrote the formula $O{=}P(OH)_2$, but he later gave up this idea after he had prepared four sodium salts:

Primary.	Secondary.	Tertiary.	Quaternary.
$MH_3P_2O_6$	$M_2H_2P_2O_6$	$M_3HP_2O_6$	$M_4P_2O_6$

and he accepted J. Volhard's suggestion that hypophosphoric acid is formed by the condensation of a mol each of phosphorous and phosphoric acids by the elimination of water: $(HO)_2{=}PO{-}\boxed{OH{+}H}O{-}P(OH)_2{\rightarrow}H_2O{+}(HO)_2P.O.P(OH)_2$. Assuming that the phosphorus in phosphorous acid is quinquevalent, this becomes $(HO)_2:PO{-}H{+}OH{-}PO:(OH)_2{=}H_2O{+}(HO):$



T. Salzer quoted the action of bromine on the acid: $Na_4P_2O_6{+}Br_2{+}H_2O{=}2NaBr{+}Na_2H_2P_2O_7$, in support of this hypothesis. According to W. Rosenheim and co-workers, the f.p. curve of mixtures of phosphorous and phosphoric acids, Fig. 37, lends no support to J. Volhard's hypothesis, since it shows no signs of the formation of a chemical compound or an isomorphous mixture of the two acids; and hypophosphoric acid cannot be formed by fusing together these two acids by some such reaction as that symbolized $H_3PO_3{+}H_3PO_4{=}H_2O{+}H_4P_2O_6$. Hence, while mixtures of phosphoric and phosphorous acids behave like mixtures, hypophosphoric acid behaves like a chemical individual. Reviewing the main arguments which have been advanced in support of one or other of the hypotheses as the mol. formula of hypophosphoric acid—H_2PO_3, or $H_4P_2O_6$—there is (1) T. Salzer's reported series of primary, secondary, tertiary, and quaternary salts. (2) A. Joly found that the heat of neutralization of hypophosphoric acid agrees better with a dibasic acid, H_2PO_3, than with a tetrabasic acid, $H_4P_2O_7$. On neutralizing hypophosphoric acid with potassium hydroxide, methyl-orange changes in tint when one eq. of potassium has been added per eq. of phosphorus; litmus changes with 1·5 eq. of potassium under the same conditions; and phenolphthalein commences to change tint with 1·5 of potassium, and the change is completed when two eq.

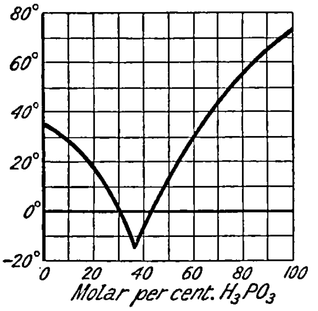


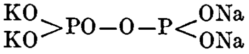
FIG. 37.—Freezing-point Curves of Mixtures of Phosphorous and Phosphoric Acids.

of potassium have been added. (3) H. Dufet considers that the isomorphism of sodium pyro- and hypophosphates agrees with the assumption that they have similar formulæ. The crystalline forms certainly have a quasi-identity, but even if the crystals are really isomorphous, the formulæ of the salts are not chemically analogous, for neither $Na_4P_2O_6.10H_2O$ nor $Na_2PO_3.5H_2O$ resembles $Na_4P_2O_7.10H_2O$. With the doubled formula for sodium hypophosphate, these salts have the same number of sodium and phosphorus atoms per mol, and approximately the same crystalline form, sp. gr., and mol. vol. (4) N. Parravano and C. Marini have argued in favour of the doubled formula $Na_4P_2O_6$ because the salts $Na_4P_2O_6.MoO_3$; $Na_4P_2O_6.2MoO_3$; $Na_4P_2O_6.3MoO_3$; and $Na_4P_2O_6.4MoO_3$ furnish anions $P_2O_6.MoO_3$; $P_2O_6.2MoO_3$; etc. The argument is a *non sequitur* because it might also be said that $2PO_3$ is always united with at least a mol. eq. of MoO_3. (5) A. Rosenheim and J. Pinsker compared the electrical conductivity μ of phosphoric, phosphorous, hypophosphorous, and hypophosphoric acids, and found

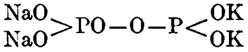
	Phosphoric acid.	Hypophosphoric acid.	Phosphorous acid.	Hypophosphorous acid.
Dilution, $v=16$ . .	124	184	222	245
Dilution, $v=1024$.	341	370	358	367

and hence inferred that the formula is probably H_2PO_3. The opposite conclusion might be inferred by comparing the conductivity of the acid regarded as $H_4P_2O_6$, with pyrophosphoric acid, $H_4P_2O_7$, for at dilution $v=1024$, μ is respectively 608 and 616. Opposite conclusions have also been drawn by A. Rosenheim, W. Stadler, and F. Jacobsohn from measurements of the conductivities of the phosphorus acids to those drawn by N. Parravano and C. Marini, and E. Cornec applied to the two sodium salts, $Na_2H_2P_2O_6$ and $Na_4P_2O_6$, points to the tetrabasic formula, $H_4P_2O_6$. (6) According to A. Rosenheim and J. Pinsker, the f.p. of aq. soln. of hypophosphoric acid and its salts resemble those of pyrophosphoric acid and its salts, and correspond with the formula $H_4P_2O_6$; but it has been argued that this molecular weight really represents associated mols. $(H_2PO_3)_2$ and not the mol. $H_4P_2O_6$ of a tetrabasic acid. (7) E. Cornec found that the progressive neutralization of the acid by potassium hydroxide gives a well-defined minimum corresponding with $K_4P_2O_6$. (8) R. G. van Name and W. J. Huff found that the speed of hydrolysis of the acid favours the assumption that the mol formula is $H_4P_2O_6$. (9) P. Walden found the formula connecting the heat of fusion and the surface tension with the mol. wt. is in agreement with the formula H_2PO_3. (10) A. Rosenheim and co-workers also found that the effect of methyl pyrophosphite, $(CH_3)_2PO_3$, and ethyl pyrophosphite, $(C_2H_5)_2PO_3$, on the b.p. of ethyl iodide or bromide, or chloroform, is in agreement with the simpler formula H_2PO_3 in place of $H_4P_2O_6$. Against this argument, however, E. Cornec has shown that there is probably a decomposition of the ethers at the b.p., and he found that the methyl ester lowered the f.p. of benzene as if its mol. weight were between 220 and 236, in agreement with the formula $(CH_3)_4P_2O_6$—theory 218. Even if the ethers did have the simpler formula, it would make it more probable but would not prove that the acid had the simpler formula because M. Meslans found that the hydrofluoric ethers—*e.g.* ethyl fluoride —have the simple formulæ RF, while the acid itself has probably the doubled formula H_2F_2. The cryoscopic behaviour of the free acid, as well as that of the potassium salt, is in agreement with the doubled formula for hypophosphoric acid. A. Rosenheim and J. Pinsker added that the higher value for the mol. wt. of this acid deduced from the cryoscopic observations, is due to the association of the simpler mols., H_2PO_3, because the mol. conductivity of aq. soln. is abnormally high if the formula is taken as $H_4P_2O_6$, and the figures so obtained ($\mu=267\cdot4$ for $v=31\cdot6$; $\mu=608\cdot8$ for $v=1111\cdot2$) are not in accordance with the properties of hypophosphoric acid. Moreover, the mol. conductivity can be brought into line with the mol. conductivities of the other acids of phosphorus only when the formula is taken as H_2PO_3. R. G. van Name and W. J. Huff do not agree with this—*vide infra*, electrical conductivity.

The fact that phosphorus tetroxide, P_2O_4, furnishes phosphoric and phosphorous acids when treated with water is expressed by the structural formula $O{=}P{\equiv}O_3{\equiv}P$. If phosphorus tetroxide be the anhydride of hypophosphoric acid—*vide supra*—it might be anticipated that $O{=}P{\equiv}O_3{\equiv}P+2H_2O \rightarrow O(OH)_2P-O-P(OH)_2$. If the last formula really represented the structure of hypophosphoric acid, it would follow that (i) this acid would be a reducing agent like phosphorous acid, but it is not; and that (ii) it ought to be possible to prepare at least two isomers by the action of sodium hydroxide on dipotassium hypophosphate, and of potassium hydroxide on disodium hypophosphate, say:

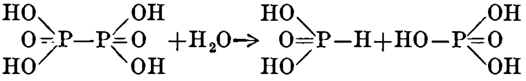


$$\begin{matrix}KO\\KO\end{matrix}\!>\!PO-O-P\!<\!\begin{matrix}ONa\\ONa\end{matrix}$$



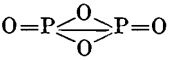
$$\begin{matrix}NaO\\NaO\end{matrix}\!>\!PO-O-P\!<\!\begin{matrix}OK\\OK\end{matrix}$$

where in one case the KO-radicles are united to quinquevalent phosphorus, and in the other to tervalent phosphorus; other isomers should also be possible. As a matter of observation, the solubility, crystalline form, action of heat, water of crystallization, of the dipotassium disodium hypophosphate prepared in different ways are "völlig identisch." With the symmetrical formula, the decomposition into phosphoric and phosphorous acids is well represented by the following scheme:



Hypophosphoric acid. Phosphorous acid. Phosphoric acid.

phosphorus tetroxide also decomposes into the same two acids in contact with cold water, and this would favour the symmetrical structure:



With two mols. of water, such an acid would give hypophosphorous acid; and with three mols. of water, a mixture of phosphoric and phosphorous acids. The mol. formula of the acid cannot be established by graphic diagrams, even if it be so demonstrated that such a formula is in harmony with the generally accepted valency of phosphorus. The formula H_2PO_3 seems to require the unusual assumption that phosphorus is quadrivalent, $O{=}P{=}(OH)_2$, although inorganic chemists have sometimes stretched the valency hypothesis as occasion demands. The evidence is indecisive.

Two hydrated hypophosphoric acids have been reported. A. Joly found that when an aq. soln. of the acid is evaporated to dryness in vacuo, crystals of **dihydrated hypophosphoric acid,** $H_4P_2O_6.2H_2O$, are formed. The four-sided, rectangular plates are probably rhombic. They are very deliquescent, and are very soluble in water. They lose their water of crystallization in vacuo, and form the anhydrous acid. Assuming that hypophosphoric acid, $H_4P_2O_6$, m.p. 70°, corresponds with the above formula, $(OH)_2OP-PO(OH)_2$, the hydrate $H_4P_2O_6.2H_2O$, melting at 62°, is sometimes regarded as a kind of *orthohypophosphoric* acid: $(HO)_4P-P(OH)_4$, and the ordinary acid as *metahypophosphoric acid*, $(HO)_2OP-PO(OH)_2$. The dihydrate melts at 62°–62·5°—A. Rosenheim and M. Pritze gave 62°. A. Joly added that the undercooled liquid gradually deposits a mass of snow-like crystals of what is probably the anhydrous acid. The mother-liquor no longer solidifies completely when seeded by a crystal of the original hydrate. If the dihydrate is kept over sulphuric acid, it effloresces, forming a mass whose m.p. falls to 55°—that of the anhydrous acid. If kept away from moisture, the dihydrate is quite stable. Water decomposes the acid into a mixture of phosphoric and phosphorous acids. If the dihydrate be kept in the molten state for some time, it gradually decomposes, and the mother-liquor remaining after crystallization contains phosphorous acid. According to A. Sänger, **monohydrated hypo-**

phosphoric acid, $H_4P_2O_6.H_2O$, is obtained in cubical crystals, when the aq. soln. is evaporated over sulphuric acid in a vacuum. The hydrate melts between 79·5° and 81·5°, and decomposes, forming a mixture of phosphoric and phosphorous acids. The mother-liquor contains some phosphorous and phosphoric acids. A. Joly suggested that this hydrate is really a mixture of the anhydrous acid and the dihydrate, and is not a chemical individual. A. Rosenheim and M. Pritze also say that the existence of this hydrate is doubtful; and that the only stable hydrate between 0° and 60° is the dihydrate. J. Kendall and co-workers studied the relations of these hydrates with those of related acids.

As previously indicated, small crystals of the anhydrous acid, $H_4P_2O_6$, are formed by drying the dihydrate in vacuo. A. Rosenheim and M. Pritze could not obtain the anhydrous acid. According to A. Joly, the acid is hygroscopic, and melts at 55°, forming a colourless, transparent liquid which completely solidifies when seeded with a fragment of the original solid. If the temp. be allowed to rise suddenly to about 70°, the acid suddenly decomposes with a considerable rise of temp.—say to 99·5°—into a mixture of metaphosphoric and phosphorous acids without loss of weight: $H_4P_2O_6=H_3PO_3+HPO_3$. Water is evolved when the acid is heated over 100°, and phosphine comes off about 180°. T. Salzer found that the sp. gr. of the aq. soln. of the acid containing the eq. of 4·1 and 12·3 per cent. PO_4 are respectively 1·036 and 1·122. According to A. Joly, the heat of fusion of the anhydrous acid is 3·85 Cals., and of the dihydrate, —4·4 Cals.; the heat of soln. of the crystalline dihydrate is —1·1 Cals. A. Joly found that the heats of neutralization of an aq. soln. of the acid with soda-lye, H_2PO_3+N-NaOH at 10°–11° are:

NaOH	0·5*N*-	*N*-	1·5*N*-	2*N*-	3*N*-
Heat evolved	7·57	15·05	21·36	27·11	27·65 Cals.

Since the heat developed by the 1st, 2nd, and 3rd eq. of alkali progressively increases, it would appear as if the acid here behaves as if it were dibasic. E. Cornec examined the effect of the progressive neutralization of hypophosphoric acid by potassium hydroxide on its f.p., and the resulting curve is lowered down to that required for the normal salt, $K_4P_2O_6$. There are breaks in the curve indicating the existence of the primary, secondary, tertiary, and quaternary salts. Analogous results were obtained with aq. ammonia and hypophosphoric acid. The behaviour of the acid is very similar to that of pyrophosphoric acid.

Measurements of the electrical conductivity of hypophosphoric acid were made by N. Parravano and C. Marini, by A. Rosenheim and J. Pinsker, and R. G. van Name and W. J. Huff. For soln. with a mol of the acid in v litres of water, J. Pinsker found at 25·6°:

v	8	16	32	64	128	256	512	1024
μ	153·8	173·6	187·2	218·2	242·0	268·8	298·4	319·0

According to R. G. van Name and W. J. Huff, these results are somewhat too low. The acid is more or less hydrolyzed. At the lower dilutions, the conductivity of the pure acid is larger than an eq. mixture of phosphorous and phosphoric acids, while at higher dilutions, this relation is reversed. A. Rosenheim and J. Pinsker argued that the mol. conductivity, referred to the H_3PO_3-formula, is of the same order of magnitude as the mol. conductivities of phosphorous and phosphoric acids:

	v	16	32	64	128	256	512
μ	H_3PO_3	222	257	292	318	337	351
	H_3PO_4	124	156	195	240	279	317
	Mean	173	206·5	243·5	279	308	334

and seems to tend on dilution towards the same limit. This tendency is to be expected if the normal mol. were H_2PO_3 since the anions HPO'_3, $H_2PO'_3$, and $H_2PO'_4$ on account of their similarity in structure would probably have nearly the same velocities. R. G. van Name and W. J. Huff showed that the phenomenon is equally well explained by the $H_4P_2O_6$-formula. Owing to the high velocity of the hydrogen ion, the conductivity of $\frac{1}{2}(H^{\cdot}+H^{\cdot}+H_2P_2O''_6)$ would be nearly the same as that of $(H^{\cdot}+HPO'_3)$. That two and only two of the eq. of hydrogen in the mol. $H_4P_2O_6$, are extensively ionized is indicated by the fact that two of these eq. of hydrogen, but not the third, can be titrated in the presence of methyl-orange. On the assumption that the anion is HPO'_3, A. Rosenheim and W. Reglin found the transport number to be 0·425 with a 0·1*N*-soln. of $NaHPO_3.3H_2O$, at 16°. The transport number at 16° is 25·4, and at 25°, 31·6.

The conc. soln. of hypophosphoric acid is a syrupy liquid which tastes acid. P. Schulz said that the hypophosphates act as poisons. According to A. Rosenheim and J. Pinsker, the acid reacts as if it were monobasic towards alkali hydroxides, using methyl-orange as indicator and as if it were hemitribasic with phenolphthalein. T. Salzer found that **hydrogen** *in statu nascendi*—from zinc and sulphuric acid—has no action. The soln. of purified hypophosphoric acid in **water** can be kept for a time, and even boiled without change, but when the soln. is conc., decomposition takes place if the temp. exceeds 30°. With long keeping, however, the acid is hydrolyzed: $H_4P_2O_6+H_2O=H_3PO_3+H_3PO_4$. A 5 per cent. soln. did not contain a trace of hypophosphoric acid after being kept for 3 years. The hydrolysis thus yields an equimolar mixture of phosphorous and phosphoric acids; it is non-reversible; it is accelerated by acids; and since soln. of acidic sodium hypophosphate are stable at room temp. for long periods, the $H^{\cdot}$-ion conc. is below the turning-point of methyl-orange, 10^{-4}, and the hydrolysis at moderate temp. is negligible. Distinctly alkaline soln. are more stable. R. G. van Name and W. J. Huff measured the speed of hydrolysis in the presence of hydrochloric acid at 25° and 60°, and found that in dil. soln. where the hydrogen ion conc. is approximately normal, the reaction is unimolecular: $H_4P_2O_6+H_2O=H_3PO_3+H_3PO_4$, and not $2H_2PO_3+H_2O=H_3PO_3+H_3PO_4$. The mean value of the velocity coeff. rises from 0·000186 at 25° to 0·00631 at 60°. In general, the results of the hydrolytic decomposition of hypophosphoric acid cannot be ignored except in special cases where temp., acidity, conc., and time have exceptionally low values. Acid soln. of hypophosphates cannot be boiled without loss, nor can they safely be conc. by heat, and even at room temp. there will be serious danger of loss (*a*) in soln. containing a large excess of other mineral acids, and (*b*) when the hypophosphate itself is present in high conc., as is the case, for example, in conc. soln. of pure hypophosphoric acid. According to A. Sänger, A. Rosenheim and M. Pritze, and J. Kendall and co-workers, there are indications of the formation of a *monohydrate*, $H_4P_2O_6.H_2O$, and of a *dihydrate*, $H_4P_2O_6.2H_2O$. The acid is not affected by **hydrogen dioxide.** Indeed, hypophosphoric acid is to be regarded only as a very weak reducing agent. The **halogens,** at atm. press., do not change the free acid. The aq. soln. of hypophosphoric acid is not changed in the cold by the mineral **acids**; but when the temp. is raised, hydrolysis occurs and phosphorous and phosphoric acids are formed. No perceptible change occurs when hypophosphoric acid is treated with **hydrogen sulphide,** or with **sulphur dioxide**; and dil. **sulphuric acid** slowly hydrolyzes hypophosphoric acid when the soln. is boiled. The dil. soln. is not affected by dil. **nitric acid,** even when boiled; if the soln. is evaporated, however, nitric acid breaks down the hypophosphoric acid, and oxidizes the liberated phosphorous acid.

According to T. Salzer, **sodium chloride** makes the soln. slowly become turbid owing to the formation of the sparingly soluble sodium hypophosphite; **sodium sulphate** behaves similarly. A white precipitate is quickly produced on adding **sodium acetate** to the acid. The blue precipitate produced by **copper sulphate** does not change its colour when boiled. The white precipitate produced by **silver nitrate** is not discoloured by boiling, and unlike the corresponding precipitates with phosphorous and hypophosphorous acid, does not blacken on exposure to light; gold chloride is not reduced. White precipitates are produced with **lime-water,** and **baryta-water**; while **calcium and barium chlorides** do not give a precipitate. With a soln. of **magnesium sulphate**, a precipitate is produced when ammonia is added—the precipitate dissolves when ammonium chloride is added. A precipitate is produced with **zinc sulphate** when ammonia is added, and the precipitate is soluble in an excess of ammonia. A soln. of **mercuric chloride** gives no precipitate and is not reduced; but, added L. Amat, if the soln. is warmed, mercurous chloride is precipitated, probably because of the splitting of hypophosphoric acid into phosphorous and phosphoric acids. T. Salzer found that soln. of *mercurous and mercuric nitrates* give white precipitates which do not change in colour in boiling soln. A soln. of **potash-alum** behaves like zinc sulphate. A soln. of *lead nitrate* or *lead acetate* gives a white precipitate. A soln. of **potassium dichromate** is not reduced even by boiling hypophosphoric acid. N. Parravano and C. Marini found that complex salts are produced by **molybdates** and **tungstates**, but the salts were not isolated; T. Salzer found that a mixture of ammonium molybdate and hydrochloric acid gives no precipitate in cold or hot soln., but when the hot soln. is mixed with nitric acid, the yellow precipitate characteristic of the phosphates is formed. A soln. of a **permanganate** is slowly reduced in the cold and rapidly when heated in the presence of dil. sulphuric acid. A soln. of **ferrous sulphate** gives a small precipitate; and a soln. of **ferric chloride,** a copious white precipitate. A soln. of **platinic chloride** gives no precipitate and is not reduced by hypophosphoric acid.

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§ 22. The Hypophosphates

In 1877 and subsequent years, T. Salzer[1] prepared the primary, secondary, tertiary, and quaternary salts as well as some more complex types. Some of the hypophosphates are obtained by saturating the acid with the base, and others by double decomposition of, say, the barium salt with a sulphate of the required base. The alkali salts are usually soluble in water, while the secondary sodium salt, the barium, and the silver salts, and the salts of the heavy metals are but sparingly soluble in water. The salts, in general, behave like the phosphites and hypophosphites, but they are much more stable, and require a higher temp. for decomposition. When heated, they usually break down, giving off hydrogen or phosphine, and leaving behind a phosphide or phosphate or a mixture of the two—silver hypophosphate gives silver and the metaphosphate. J. Palm prepared manganese, iron, chromium, aluminium, acid bismuth hypophosphates in a similar way. P. Drawe, J. Palm, and C. Bansa prepared isomorphous, rhombic crystals of the acidic double salts of the type $M''H_2P_2O_6.K_2H_2P_2O_6.nH_2O$, where M″ denotes an atom of a bivalent metal—nickel, cobalt, cadmium, manganese, zinc, and copper—also normal double salts $M''K_2P_2O_6.nH_2O$, where M″ denotes an atom of bivalent cobalt or nickel. Double salts with sodium in the place of potassium were also obtained.

A. Sänger prepared *ethyl hypophosphate*, $(C_2H_5)_4P_2O_6$, as a thick, colourless liquid of sp. gr. 1·117 at 15°, by heating silver hypophosphate with ethyl iodide. The ester is hydrolyzed by water, and decomposes, when heated, into ethyl phosphate and phosphite. Consequently, the vapour density cannot be determined. The corresponding *methyl hypophosphate*, $(CH_3)_4P_2O_6$, has a sp. gr. 1·109 at 15°. Both esters form a calcium salt, $RCaHP_2P_6.5H_2O$. A. Rosenheim, W. Stadler and F. Jacobsohn could not prepare ethyl hypophosphate because it so readily passed into ethyl pyrophosphate. A. Rosenheim and J. Pinsker also prepared white needle-like crystals of a characteristic sparingly soluble *guanidine hypophosphate*, $(CN_3H_5)_4H_2PO_3.5H_2O$, by treating guanidine carbonate with a soluble hypophosphate or the free acid; and I. Müller showed that if hot conc. soln. are mixed, the precipitated salt has the composition $(CN_3H_5)_2PO_3.H_2O$.

T. Salzer prepared normal or quaternary **ammonium hypophosphate,** $(NH_4)_4P_2O_6.H_2O$, by treating a 5 per cent. soln. of hypophosphoric acid with an excess of ammonia. The prismatic crystals effloresce so quickly by the loss of ammonia in air that measurements of the crystallographic constants were not practicable. 100 grms. of water dissolve 3·3 grms. of the salt. The aq. soln. has a strong alkaline reaction; it gives no precipitate with ammonia; it loses ammonia when evaporated and becomes acid, furnishing the secondary salt. T. Salzer obtained the secondary salt **ammonium dihydrohypophosphite,** $(NH_4)_2H_2P_2O_6$, by over-saturating the acid with aq. ammonia, and allowing the soln. to evaporate spontaneously. If the soln. is such that no more ammonia escapes during evaporation, some primary salt may be formed. A. P. Sabanéeff evaporated the soln. obtained by neutralizing the free acid with ammonia, using methyl-orange as indicator; and T. Salzer, the soln. obtained by the double decomposition of the secondary barium salt with ammonium sulphate. The granular or acicular crystals lose neither water nor ammonia at 110°; and the salt can be heated to 160° for an hour without appreciable decomposition, but at a higher temp., decomposition occurs. A. P. Sabanéeff gave 170° for the m.p., and found the mol. wt. by cryoscopic observations of the aq. soln. in agreement with the formula indicated, so that the salt is structurally isomeric with hydrazine hydrophosphite. T. Salzer found that 100 grms. of water at 14° dissolve 7·1 grms. of salt, and at the boiling temp., 25 grms. If a soln. of this salt with the necessary quantity of acid be evaporated on a water-bath, and allowed to crystallize in a desiccator, granular crystals of the primary salt, **ammonium trihydrohypophosphate,** $(NH_4)H_3P_2O_7$, are formed. This salt is very soluble in water; it melts at a lower temp. than the dihydro-salt, but otherwise behaves in a similar way.

A. P. Sabanéeff prepared **hydroxylamine dihydrohypophosphate,** $(NH_3OH)_2H_2P_2O_6$, by crystallization from a soln. obtained by mixing the barium salt with hydroxylamine hydrosulphate. The salt is structurally isomeric with hydrazine dihydrophosphate; it melts with decomposition at 139°; and is freely soluble in water. He prepared **hydrazine dihydrohypophosphate,** $(N_2H_5)_2H_2P_2O_6$, by crystallization from a soln. of the acid neutralized with hydrazine hydrate using methyl-orange as indicator. The prismatic crystals are freely soluble in water. If half of a given amount of hypophosphoric acid be neutralized as just indicated, and mixed with the other portion of acid, the soln. furnishes crystals of **hydrazine trihydrohypophosphate,** $(N_2H_5)H_3P_2O_6$. The salt is structurally isomeric with ammonium dimetaphosphate; it melts at 152°; and, at ordinary temp., 100 grms. of water dissolve 1·5 grms. of the salt. If the aq. soln. of this salt be neutralized with ammonia, using methyl-orange as indicator, and the soln. allowed to crystallize without warming, **hydrazine ammonium dihydrohypophosphate,** $(NH_4)(N_2H_5)H_2P_2O_6$, is obtained in small crystals, readily soluble in water.

According to C. F. Rammelsberg, and T. Salzer normal **lithium hypophosphate,** $Li_4P_2O_6.7H_2O$, is obtained by mixing soln. of the normal sodium salt and lithium chloride in the molar proportions 1 : 2 ; and by adding sufficient lithium carbonate to hypophosphoric acid to give a liquid which still has an acid reaction. H. Schuh regarded this salt as a hexahydrate. A. Rosenheim and W. Reglin gave for the sp. conductivity of a sat. soln. at 25°, $2{\cdot}772\times10^{-4}$ mho. C. F. Rammelsberg said that the salt can be recrystallized from a hot conc. soln. in water and acetic acid. The crystals lose 5 mols of water at 120°, and 6 mols at 300°. The salt is sparingly soluble in water—C. F. Rammelsberg said that at ordinary temp. 100 grms. of water dissolve 0·83 grm. of the salt. A. Rosenheim and W. Reglin observed a negative temp. coeff. of the solubility, for at 0°, 25°, and 40°, 100 grms. of a sat. soln. contained respectively 0·1018, 0·0575, and 0·0480 grm. of $Li_4P_2O_6.7H_2O$. The salt is easily soluble in hypophosphoric acid. The mother-liquor from the normal salt yields ill-defined crystals of **lithium dihydrohypophosphate,** $Li_2H_2P_2O_6.2H_2O$. H. Schuh regarded it as a tetrahydrate. I. Müller has investigated the conditions of equilibrium of the ternary system, $Na_2O{-}P_2O_4{-}H_2O$, at 30°, and his numbers are plotted in Fig. 38. The point *A* corresponds with a sat. soln. of $NaHPO_3.3H_2O$, or $Na_2H_2P_2O_6.6H_2O$, and the curve *AB* must correspond with the appearance of a second salt, otherwise the addition of soda-lye to a sat. soln. of $NaHPO_3.3H_2O$ would lower the solubility. This salt is T. Salzer's $Na_3HP_2O_6.9H_2O$, or $Na_3H(PO_3)_2.9H_2O$; *B* represents the solubility of a sat. soln. of this salt. The behaviour of the curve *BCD* (allowing for errors of experiment) corresponds with the formation of T. Salzer's $Na_5H_3(P_2O_6)_2.20H_2O$, but the salt was not isolated. The curve *DE* corresponds with the appearance of needle-like crystals of the salt $Na_2PO_3.5H_2O$, or T. Salzer's $Na_4P_2O_6.10H_2O$. The kink *H* in the curve *AG* corresponds with the salt $Na_3H_5(P_2O_6)_2.nH_2O$—the sodium analogue of T. Salzer's $K_3H_5(P_2O_6)_2.2H_2O$—but the salt was not isolated. Under the conditions of these experiments, therefore, four salts—$Na_4P_2O_6.10H_2O$; $Na_3HP_2O_6.9H_2O$; $Na_2H_2P_2O_6.6H_2O$; and $NaH_3P_2O_6.2H_2O$—can exist in aq. soln. at 30° ; while the salts, $Na_5H_3(P_2O_6)_2.20H_2O$, and $Na_3H_5(P_2O_6)_2.nH_2O$, could not be obtained, though there were indications of their presence.

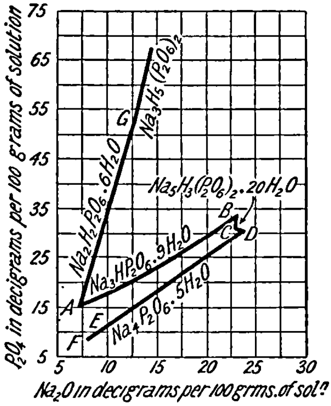

FIG. 38.—Equilibrium in the Ternary System: $Na_2O{-}P_2O_4{-}H_2O$.

T. Salzer, C. F. Rammelsberg, and H. Schuh prepared acicular crystals of the decahydrated normal **sodium hypophosphate,** $Na_4P_2O_6.10H_2O$, by cooling a boiling soln. of equimolar parts of sodium dihydrohypophosphate and sodium carbonate; if an excess of conc. soda-lye be rapidly added to a soln. of one part of the dihydro-salt in 50 parts of water, the salt is immediately precipitated, if the soda-lye be not in excess, the soln. remains clear, and the crystals are deposited by gradually adding more lye. The range of stability is indicated in Fig. 38. The six-sided monoclinic crystals were found by W. Fresenius to have the axial ratios $a:b:c$ $=2{\cdot}0435:1:1{\cdot}9099$; while H. Dufet gave $1{\cdot}1718:1:1{\cdot}9077$, and $\beta=79°\ 44'$, and sp. gr. 1·8233. T. Salzer found that when the salt is heated, it decomposes without incandescence, forming a reddish-coloured mass, which gives a turbid yellowish-red soln. in water. If the tetrasodium salt is heated, it passes into the pyrophosphate, while the disodium salt forms the metaphosphate—it is therefore possible to determine the proportions of the di- and tetra- sodium hypophosphates in a mixture of the two on the assumption that each constituent of the mixture behaves like it would alone. 100 parts of water dissolve 2 parts of the salt. I. Müller gave for the solubility of the anhydrous salt in 100 grms. of water:

	25·2°	30°	35°	40·2°	45°	50°
Solubility .	1·49	1·72	1·96	2·27	2·71	3·18 grms.

T. Salzer found that the aq. soln. reacts alkaline, and colours turmeric brown, and, said A. Joly, phenolphthalein, red. T. Salzer added that the salt cannot be recrystallized from water without change. Bromine changes the aq. soln. into the dihydropyrophosphate: $Na_4P_2O_6+Br_2+H_2O=Na_2H_2P_2O_7+2NaBr$. T. Salzer said that in preparing the normal salt, sometimes a small quantity of a salt of the same composition is formed; it is almost insoluble in water. It has not been examined, and was provisionally regarded as a polymer. If a mol of sodium carbonate, and 4 mols of the dihydro-salt, be dissolved in water and boiled until carbon dioxide is no longer evolved, rhombic plates of **sodium trihydrodihypophosphate,** $Na_5H_3(P_2O_6)_2.20H_2O$, separate on cooling. The range of stability is indicated in Fig. 38. K. Haushofer said that the monoclinic crystals have the axial ratios $a:b:c=1·3638:1:0·5761$, and $\beta=78° 38'$. T. Salzer added that 100 parts of water dissolve 6·7 parts of the salt; the soln. is only feebly acid; and on evaporation furnishes crystals of the dihydro- and trihydro-salts. I. Müller suspected the existence of **sodium pentahydrodihypophosphate,** $Na_3H_5(P_2O_6)_2$, with the very limited range of stability indicated in Fig. 38.

T. Salzer prepared **sodium hydrohypophosphate,** $Na_3HP_2O_6.9H_2O$, from a soln. of a mol of the dihydro-salt with 0·5 mol of sodium carbonate, or a mol of the normal salt. The range of stability is indicated in Fig. 38. The clear, colourless crystals are usually tabular, and, according to H. Dufet, belong to the monoclinic system, having the axial ratios $a:b:c=1·5592:1:1·5108$; $\beta=77° 33'$; and the sp. gr. 1·7427. T. Salzer added that the salt loses its water of crystallization at 100°, and at a higher temp. glows and gives off phosphine. The crystals do not effloresce in air; 100 parts of water dissolve 4·5 parts of salt. According to I. Müller, 100 grms. of water dissolve *S* grms. of the anhydrous salt:

	25°	30·2°	35·2°	40°	45°	50°
Solubility .	4·67	5·88	7·16	9·00	11·85	14·96 grms.

T. Salzer said that the aq. soln. is alkaline, and, according to A. Joly, gives a pale violet colour with phenolphthalein. T. Salzer, and H. Schuh prepared **sodium dihydrohypophosphate,** $Na_2H_2P_2O_6.6H_2O$, from hypophosphoric acid as previously indicated in connection with the acid. The range of stability is indicated in Fig. 38. A. Joly obtained it from a soln. of hypophosphoric acid neutralized with sodium carbonate until a methyl-orange indicator reddens. The monoclinic crystals are often monoclinic. K. Haushofer gave for the axial ratios $a:b:c=2·0052:1:2·0568$, and $\beta=52° 33'$; while C. R. Fresenius gave $a:b:c=2·0115:1:2·0438$, and $\beta=53° 10·5'$. H. Dufet added that the birefringence is positive, and the sp. gr. 1·8491. According to T. Salzer, the clear crystals remain unchanged at ordinary temp., but over conc. sulphuric acid, or in contact with alcohol, they lose water and become turbid. At 100°, the water of crystallization is expelled, and the salt suffers no further change at 200°, but at 250° the salt melts, and at higher temp. gives off phosphine and hydrogen, and forms sodium phosphide as well. When heated in an atm. of carbon dioxide, no phosphine is given off. 100 grms. of cold water dissolve 2·2 grms. of the salt, and boiling water, 20 grms. I. Müller gave for the solubility of the dihydro-salt in 100 grms. of water:

	25°	30°	35°	40°	45°	50°
Solubility . .	2·00	2·57	3·08	3·77	4·76	5·95

The results are indicated in Fig. 36. According to T. Salzer, the aq. soln. has an acid reaction, and is stable in air; the salt dissolves more easily in dil. sulphuric acid than in water; it is freely soluble in aq. ammonia; and not so soluble in a soln. of sodium carbonate. N. Parravano and C. Marini, and A. Rosenheim and W. Stadler measured the electrical conductivity of soln. of the sodium salts; A. Rosenheim and W. Reglin gave for the eq. conductivity, λ, with a mol of the salt, $Na_2H_2P_2O_6.6H_2O$, in v litres of water at 25°:

v	8	16	32	64	128	256	512	1024
λ	71·8	78·8	86·1	92·2	95·9	98·1	100·7	101·6

T. Salzer prepared **sodium trihydrohypophosphate,** $NaH_3P_2O_6$, by slowly cooling a hot conc. soln. of the dihydro-salt mixed with some hypophosphorous acid. I. Müller also obtained this salt. According to K. Haushofer, the acicular or tabular crystals are monoclinic with the axial ratios $a:b:c=2·0023:1:1·0907$, and $\beta=82° 41'$. The aq. soln. deposits crystals of the dihydro-salt. When heated, the salt melts in its water of crystallization, and at a higher temp., the salt decrepitates and gives off hydrogen which ignites.

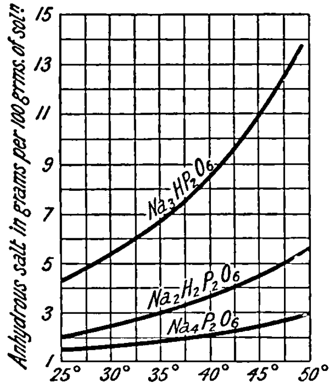

FIG. 39.—The Solubility of the Sodium Hypophosphates in Water.

T. Salzer prepared primary or normal **potassium hypophosphate,** $K_4P_2O_6.8H_2O$, by adding 2 mols of potassium hydroxide to a soln. containing one mol of the dihydro-salt, and evaporating to a syrupy liquid on the water-bath, and finally in a desiccator. C. Bansa said that the salt cannot be prepared by double decomposition of the barium salt with potassium sulphate because the reaction is an incomplete one. K. Haushofer said that the prismatic or tabular crystals are rhombic pyramids with a tetragonal habit, and have the axial ratios $a:b:c=0·9458:1:1·0124$. T. Salzer found that 100 grms. of water dissolve rather more than 25 grms. of the salt. The soln. is alkaline, and does not absorb carbon dioxide from the air. The salt melts at about 40° in its water of crystallization; it loses three-quarters of its water at 60°, and the remainder at 150° without decomposition; but at a higher temp. it forms pyrophosphate. The salt is insoluble in alcohol, but is not precipitated by alcohol from its aq. soln. T. Salzer also found that **potassium pentahydrodihypophosphate,** $K_3H_5(P_2O_6)_2.2H_2O$, is deposited when a soln. containing 3 mols of potassium dihypophosphate and one mol of hypophosphoric acid is evaporated. If a smaller proportion of acid is used, this salt is also formed, but is apt to contain potassium trihydrohypophosphate. According to C. R. Fresenius, and K. Haushofer, the crystals belong to the rhombic system, and have the axial ratios $a:b:c=0·6792:1:0·8508$. The salt is soluble in 2·5 parts of cold and in 0·8 part of boiling water. On the addition of alcohol to the aq. soln., dipotassium hypophosphate is precipitated. The crystals become anhydrous at 100°.

T. Salzer obtained **potassium hydrohypophosphate,** $K_3HP_2O_6.3H_2O$, by the addition of equimolar parts of potassium hydroxide to a soln. of potassium dihypophosphate and evaporating for crystallization. According to K. Haushofer, the salt crystallizes in the monoclinic system, and has the axial ratios $a:b:c=0·4224:1:0·9902$, $\beta=89° 35'$. T. Salzer said that the crystals are soluble in half their weight of water, forming an alkaline soln., but are insoluble in alcohol. They lose their water of crystallization at 100°, and at a higher temp. form potassium pyro- and meta-phosphate. T. Salzer also prepared di- and tri-hydrated **potassium dihydrohypophosphates,** $K_2H_2P_2O_6.2H_2O$, and $K_2H_2P_2O_6.3H_2O$, from the soln. obtained by digesting the barium salt with a soln. of potassium sulphate. The evaporation of the filtered soln. furnishes either rhombic prisms or plates of the trihydrate which, according to K. Haushofer, have the axial ratios $a:b:c=0·9873:1;0·9190$; or monoclinic plates of the dihydrate, having the axial ratios $a:b:c=0\cdot7241:1:0\cdot7949$, and $\beta=87°\ 50'$. T. Salzer did not find a method for obtaining crystals of only one form. The trihydrate effloresces in air, the dihydrate is stable. They lose their water of crystallization at 100°, and at a higher temp. give off hydrogen which inflames; the residue contains the metaphosphate. Both salts dissolve in three times their weight of cold water, and in their own weight of hot water. They are precipitated from their aq. soln. by the addition of alcohol. These two alleged hydrates want further examination. According to T. Salzer, **potassium trihydrohypophosphate,** $KH_3P_2O_6$, is deposited during the slow cooling of a hot conc. soln. of the dihydro-salt and hypophosphoric acid. The monoclinic prisms were found by K. Haushofer to have the axial ratios $a:b:c=0\cdot9331:1:0\cdot6612$, and $\beta=43°\ 7'$. T. Salzer added that 100 parts of water dissolve 66·7 parts of salt in the cold, and when boiling, 200 parts of salt. The soln., which have an acid reaction, give a precipitate with alcohol. On spontaneous evaporation, the cold aqueous soln. yields potassium pentahydrodihypophosphate; whilst the hot soln. contains, in addition to this salt, the potassium hydrohypophosphate. The trihydrohypophosphate undergoes no change at 100°, but at 120° it absorbs moisture from the air, forming phosphorous acid and potassium pyrophosphate.

The two series of potassium and sodium salts prepared by T. Salzer are thus analogous, but he could not make the sodium analogue of $K_3H_5(P_2O_6)_2.2H_2O$, nor the potassium analogue of $Na_5H_3(P_2O_6)_2.20H_2O$. There is no evidence to show that the sodium salt, $Na_5H_3(P_2O_6)_2.20H_2O$, and the potassium salt, $K_3H_5(P_2O_6)_2.2H_2O$, are derivatives of polymerized hypophosphoric acid; they may be association products analogous with H.COOH.H.COONa; $KNO_3.2HNO_3$; etc. If the mol. constitution of the acid be H_2PO_3, this would render necessary a modification of the present view of the constitution of these salts. The quaternary sodium salt would become $Na_2PO_3.5H_2O$; and the secondary salt, $NaHPO_3.3H_2O$; while the tertiary salt, $Na_3HP_2O_6.9H_2O$, would become a double salt, $Na_2PO_3.NaHPO_3.9H_2O$; the primary salt, $NaH_3P_2O_6.2H_2O$; a double salt, $H_2PO_3.NaHPO_3.2H_2O$; and the pentasodium salt, a double salt, $Na_2PO_3.3NaHPO_3.20H_2O$. H. Schuh prepared **rubidium dihydrohypophosphate,** $Rb_2H_2P_2O_6.2H_2O$; and the normal **rubidium hypophosphate,** $Rb_4P_2O_6.10H_2O$.

T. Salzer obtained a blue precipitate on adding a soln. of cupric sulphate to hypophosphoric acid, and P. Drawe prepared **cupric hypophosphite,** $Cu_2P_2O_6.6H_2O$, by adding a warm dil. soln. of the normal salt to an excess of warm soln. of copper sulphate. The salt is insoluble in water, and soluble in dil. acids. It does not form the pyrophosphate when calcined in air. C. Bansa made **potassium copper octohydrotetrahypophosphate,** $3K_2H_2P_2O_6.CuH_2P_2O_6.15H_2O$, or $K_6CuH_8(P_2O_6)_4.15H_2O$, by adding to a conc. soln. of potassium dihydrohypophosphate a few drops of a 20 per cent. soln. of cupric sulphate. On standing a few hours, the soln. deposits pale blue, acicular, and tabular crystals of the complex salt, which melts with decomposition at 170°. T. Salzer prepared **silver hypophosphate,** $Ag_4P_2O_6$, by the action of silver nitrate on a neutral or acidic soln. of sodium hypophosphate; J. Philipp, by warming phosphorus with dil. nitric acid in the presence of silver nitrate—*vide supra*; A. Sänger, by the action of silver nitrate in neutral or feebly ammoniacal soln. on sodium hypophosphate—some silver suboxide is formed at the same time—*vide supra*; and F. Tauchert, by the action of silver nitrate on a warm soln. of sodium dihydrohypophosphate. The white salt is not very sensitive to light; and when boiled with its mother-liquor, is not discoloured. It is insoluble in water, and sparingly soluble in nitric acid; and almost insoluble in hypophosphoric acid, so that T. Salzer was unable to make an acidic salt. J. Philipp said that the salt can be recrystallized from a nitric acid soln. of silver nitrate; and A. Sänger, that the salt is oxidized to the normal phosphate by silver oxide. C. Bansa obtained crystals of **sodium potassium hypophosphate,** $Na_2K_2P_2O_6.9H_2O$, by adding the theoretical quantity of potassium carbonate to a soln. of sodium dihydrohypophosphate. The rhombic crystals have the axial ratios $a:b:c$

=1·0728 : 1 : 1·00845. The crystals do not change in air. They are soluble in about 3 parts of hot water, or 25 parts of cold water; 8 mols of water are lost at 100°, and the remainder at 260°; at 300°, the salt becomes brown, then white again, and finally melts. At a red-heat, the salt burns owing to the inflammation of the escaping hydrogen. No phosphine was detected.

T. Salzer made normal **calcium hypophosphate,** $Ca_2P_2O_6.2H_2O$, by treating a soln. of the normal sodium salt with calcium chloride. He added that a neutral soln. of a calcium salt will give a turbidity with a dilution of 1 in 20,000. The washed precipitate is not crystalline, but gelatinous, and it becomes granular after standing some time. The air-dried salt retains some moisture. The combined water is lost at 200° when some oxidation occurs. At a dull red-heat, calcium pyrophosphate is formed without the inflammation of evolved hydrogen. The salt is insoluble in water; sparingly soluble in acetic acid; and freely soluble in hydrochloric or hypophosphoric acid. If barium dihydrohypophosphate suspended in water is treated with calcium sulphate, or the normal calcium salt be treated with the theoretical quantity of hypophosphoric acid, and the clear soln. evaporated without a rise of temp., crystals of **calcium dihydrohypophosphate,** $CaH_2P_2O_6.6H_2O$, are formed. According to K. Haushofer, the monoclinic plates or prisms have the axial ratios $a:b:c=1·1342:1:2·5426$, and $\beta=94°\ 31'$. T. Salzer found that the salt loses two-thirds of its water on exposure to air, and the remainder at 150°. There is a partial decomposition of the salt at that temp. When rapidly heated the salt decomposes and the liberated hydrogen burns with a blue flame. 100 parts of water dissolve 1·7 parts of salt. H. Schuh prepared normal **strontium hypophosphate,** $Sr_2P_2O_6.2H_2O$; and **strontium dihydrohypophosphate,** $SrH_2P_2O_6.3H_2O$. T. Salzer, C. Bansa, and H. Schuh prepared normal **barium hypophosphate,** $Ba_2P_2O_6$, by treating a soln. of the normal sodium salt with barium chloride. At a red-heat, the white, pulverulent mass passes into the pyrophosphate without incandescence. C. F. Rammelsberg said that the salt dried over sulphuric acid retains 1·6 per cent. of moisture. H. E. Quantin said that the salt is decomposed by the vapour of carbon tetrachloride at a red-heat, forming barium chloride, carbonyl chloride, and carbon dioxide. T. Salzer made **barium dihydrohypophosphate,** $Ba_2H_2P_2O_6.2H_2O$, by dissolving the normal salt in the theoretical quantity of hypophosphoric acid, and evaporating for crystallization without raising the temp.; also by precipitation on mixing a soln. of 12 grms. of dihydrated barium chloride in 120 grms. of water and a soln. of 16 grms. of hexahydrated sodium dihydrohypophosphate in 100 grms. of water, and 6 c.c. of hydrochloric acid of sp. gr. 1·124. According to A. Joly, if a nearly boiling soln. of hypophosphoric acid is treated with one-quarter the amount of barium carbonate required for neutralization, on cooling, the dihydro-salt is precipitated free from phosphite and phosphate. C. F. Rammelsberg obtained the salt by evaporating a soln. of the normal salt in hydrochloric acid. The clear, needle-like crystals were found by W. Fresenius to belong to the monoclinic system, and to have the axial ratio $a:b:c=1·8480:1:$—, and $\beta=122°\ 56'$. The slimy precipitate of the barium salt, said A. Joly, is formed with thermal change, but when this passes into the crystalline salt, 4·76 Cals. are evolved. The heat of neutralization of barium hydroxide and hypophosphoric acid is 56·4 Cals. when barium dihydrohypophosphate is formed. T. Salzer said that the crystals suffer no appreciable change at 100°; at 140°, they lose their water of crystallization, and at a higher temp. hydrogen is evolved, and this inflames. Barium metaphosphate remains. When the clear crystals are heated under water, they become opaque, and the water becomes acid owing to the formation of a small quantity of the normal salt.

C. F. Rammelsberg, and J. Palm prepared crystals of normal **beryllium hypophosphate,** $Be_2P_2O_6.3H_2O$, by mixing a cold soln. of the normal sodium salt with beryllium sulphate. The pulverulent mass loses about half its water of crystallization at 230°–250°. T. Salzer made normal dodecahydrated **magnesium hypophosphate,** $Mg_2P_2O_6.12H_2O$, by mixing a cold soln. of the normal sodium salt

(1 : 100) with the theoretical quantity of magnesium sulphate—the precipitate is crystalline. If hot soln. are mixed, the precipitate is gelatinous, and crystallization then occurs only after long standing. The precipitate is washed free from sulphates. The microcrystalline, rhombic or hexagonal plates are stable in air; they lose five-sixths of their water at 110°; and at 170°, more water is given off with some decomposition of the salt. 100 parts of water dissolve 0·0067 part of salt. C. F. Rammelsberg also examined this salt, and found that if the soln. in acetic acid with a drop of hydrochloric acid be evaporated, crystals of the *tetracosihydrate* are formed which lose 12 mols of water at 200°. T. Salzer made **magnesium dihydrohypophosphate,** $MgH_2P_2O_6.4H_2O$, by digesting the barium salt with a soln. of magnesium sulphate; or by digesting a mol of the normal salt with a mol of hypophosphoric acid. The dil. soln. can be boiled without change, and crystals of the salt are obtained by evaporating the liquid. The crystals are stable in air; they lose water of crystallization at 150°; and decompose with a glow at a higher temp. 100 parts of water dissolve 0·5 part of salt—*vide supra,* the action of the acid on magnesium salts. P. Drawe prepared **zinc hypophosphate,** $Zn_2P_2O_6.2H_2O$, by stirring an excess of a dil. soln. of zinc sulphate with one of sodium dihydrohypophosphate, and after 24 hrs. filtering the soln., washing with hot water, and drying on porous tiles. The white powder at 110° becomes yellow, and at a higher temp., glows. The white product suffers a loss of 8·9 per cent. in weight. C. Bansa prepared **potassium zinc octohydrotetrahypophosphate,** $3K_2H_2P_2O_6.ZnH_2P_2O_6.15H_2O$, by mixing a few drops of a conc. soln. of zinc sulphate to one of potassium dihydrohypophosphate (1 : 3) at ordinary temp. The crystalline precipitate loses all its water after heating 4 hrs. at 100°; and melts with decomposition at 140°. P. Drawe prepared **cadmium hypophosphate,** $Cd_2P_2O_6.2H_2O$, by the method employed for the zinc salt. The product is insoluble in water, and alcohol, but freely soluble in dil. acids. The salt loses half its water of crystallization at 100°, and at 110°, it loses in weight and becomes superficially yellow. It decomposes when ignited, forming the metal phosphide. He also prepared **potassium cadmium tetrahydrodihypophosphate,** $K_2H_2P_2O_6.CdH_2P_2O_6.2\frac{1}{2}H_2O$, in rhombic crystals, by a method analogous to that employed for the zinc salt. The salt begins to lose water at 120°, but is not completely dehydrated at a red-heat. It melts at 170°. No **mercury hypophosphate** has been made; according to L. Amat, mercuric chloride oxidizes hypophosphoric acid quantitatively into phosphoric acid; and is itself reduced to mercurous chloride—*vide supra,* hypophosphorous acid.

J. Palm prepared **aluminium hypophosphate** from a soln. of the normal sodium salt and aluminium sulphate. C. F. Rammelsberg reported normal **thallous hypophosphate,** $Tl_4P_2O_6$, to be formed by neutralizing a soln. of the acid with thallous carbonate; and A. Joly, by double decomposition with thallous sulphate and a hot aq. soln. of the normal sodium salt. The colourless needles are sparingly soluble in water. A. Joly said that in direct sunlight, the salt is coloured indigo-blue; and it remains unchanged when heated to 210°, but, added A. Joly, it melts and decomposes: $Tl_4P_2O_6=2TlPO_3+2Tl$, at 250°. A. Joly made **thallous dihydrohypophosphate,** $Tl_2H_2P_2O_6$, by neutralizing a soln. of the acid with thallous carbonate, using methyl-orange as indicator, or mixing barium dihydrohypophosphate and thallous sulphate in boiling aq. soln. H. Dufet said that the monoclinic crystals have the axial ratios $a:b:c=0{\cdot}9089:1;\ 1{\cdot}2975$, and $\beta=94°\ 50'$. A. Joly said that the salt melts at 200° and forms a phosphite without the evolution of a gas. C. F. Rammelsberg reported small, colourless crystals of **thallous hydrohypophosphate,** $Tl_4P_2O_6.Tl_2H_2P_2O_6$, or $Tl_3HP_2O_6$, to be formed by mixing the soln. of hypophosphoric acid neutralized with thallous carbonate with the theoretical amount of acid, and evaporating the clear soln. O. Hauser and H. Herzfeld prepared **zirconium hypophosphate,** $ZrP_2O_6.H_2O$, by warming a soln. of zirconium nitrate in dil. hydrochloric acid with an excess of sodium hypophosphate. T. Salzer reported **lead hypophosphate,** $Pb_2P_2O_6$, to be formed by treating sodium dihydrohypophosphate with a large excess of lead nitrate, acetate, or basic acetate. H. Schuh, and F. Tauchert employed a similar process. The white, pulverulent mass is not altered at 120°, at a higher temp. it blackens, and may glow if in a thin layer; and if air has access: $Pb_2P_2O_6+O=Pb_2P_2O_7$. It is insoluble in water, dil. acetic acid, and hypophosphoric acid; but it is soluble in dil. nitric acid. It is readily decomposed by dil. sulphuric acid. O. Kauffmann prepared **thorium hypophosphate,** $ThP_2O_6.11H_2O$, by precipitation from a soln. of thorium nitrate as in the case of the zirconium salt. It is also obtained by adding hypophosphoric acid to a soln. of thorium nitrate. The white, pulverulent mass loses its water of crystallization at 160°–170°. O. Kauffmann said that it is insoluble in water, dil. acids, and alkalies, and in conc. acids, but V. I. Spitzin found N-H_2SO_4 dissolves 53 mgrms. per litre; N-HCl, 24 mgrms. per litre; N-HNO_3, 12 mgrms. per litre; and N-K_2CO_3, 250 mgrms. per litre. O. Kauffmann said that it is opened up by fusion with sodium hydrosulphate, and dissolution by hydrochloric acid.

J. Palm reported **bismuth hypophosphate** to be formed from a soln. of the normal sodium salt and bismuth nitrate. J. Palm prepared **chromium hypophosphate** from a soln. of the normal sodium hypophosphate and a chromium salt. According to N. Parravano and C. Marini, sodium hypophosphate forms complex anions with molybdic acid, represented by **sodium hypophosphatomolybdate:** $2Na_2MoO_4+H_4P_2O_6=2H_2O+Na_4P_2O_6.2MoO_3$, and I. Müller prepared the complex molybdenum salt by treating a boiling soln. of sodium hypophosphite with an excess of molybdic trioxide, MoO_3, and treating the clear greenish soln. with bromine water—pale yellow crystals of sodium hypophosphatomolybdate, $Na_2[P(Mo_2O_7)].8H_2O$, appear. N. Parravano and C. Marini also obtained evidence of the formation of a complex **sodium hypophosphatotungstate.** They measured the electrical conductivities of hypophosphatomolybdates. J. Palm reported **manganese hypophosphite** to be formed from a soln. of the normal sodium salt and manganese chloride; and C. Bansa obtained colourless, rhombic crystals of **potassium manganese tetrahydrodihypophosphate,** $MnH_2P_2O_6.K_2H_2P_2O_6.3H_2O$, as in the case of the cadmium salt. J. Palm prepared **iron hypophosphate** as in the case of the manganese salt. P. Drawe prepared **cobalt hypophosphate,** $Co_2P_2O_6.8H_2O$, by mixing a warm dil. soln. of the normal sodium salt with an excess of a warm soln. of cobalt sulphate. The salt is almost insoluble in water, and when heated, it readily oxidizes. S. Bansa made **potassium cobalt hypophosphate,** $K_2CoP_2O_6.5H_2O$, by mixing a soln. of 3 grms. of heptahydrated cobalt sulphate in 20 c.c. of hot water with a hot 5 per cent. soln. of the normal potassium salt. When the rose-coloured mass of crystals is heated, it becomes blue, and finally black. P. Drawe made six-sided plates of **sodium cobalt hypophosphate,** $Na_2CoP_2O_6.1\frac{1}{2}H_2O$, by mixing a dil. soln. of cobalt sulphate with one of the normal sodium salt at 0°. The salt is decomposed by water, forming normal cobalt hypophosphate. The salt loses weight when kept over sulphuric acid, and it becomes dark violet; it also lost 4·3 per cent. of water when kept for 3 hrs. at 110°. At a higher temp., the salt becomes deep blue and finally black. I. Müller prepared brown crystals of **sodium cobaltic hexamminohypophosphate,** $[Co(NH_3)_6]NaP_2O_6.3H_2O$, by mixing hot conc. soln. of cobaltic hexamminotrichloride and sodium hypophosphate. C. Bansa reported **hexapotassium cobalt octohydrotetrahypophosphate,** $3K_2H_2P_2O_6.CoH_2P_2O_6.15H_2O$, or $CoK_6H_8(P_2O_6)_4.15H_2O$, to be formed by mixing a soln. of 7·75 grms. of hexahydrated cobalt ammonium sulphate in 50 c.c. of water with 80 c.c. of a 25 per cent. soln. of potassium dihydrohypophosphate. The pale rose-coloured, rhombic crystals slowly lose water in the desiccator, and become blue. The salt is dehydrated at 100°, and it begins to oxidize at about this temp. The salt becomes black at 200°–300°.

P. Drawe made prismatic crystals of **nickel hypophosphate,** $Ni_2P_2O_6.12H_2O$, by the action of an excess of a warm dil. soln. of the normal sodium salt on a warm soln. of nickel sulphate; C. Bansa also obtained it by the action of potassium dihydrophosphate on an excess of nickel sulphate soln., and mixing the green filtrate with potassium acetate. C. Bansa also obtained **potassium nickel hypophosphate,** $K_2NiP_2O_6.6H_2O$, by mixing a boiling soln. of 3 grms. of hydrated nickel sulphate in 20 c.c. of water on 100 c.c. of a hot soln. of 5 grms. of normal potassium hypophosphate. After heating 6 hrs. at 100°, the salt loses one-third of its water of crystallization and becomes pale yellow; 3 mols. are lost after 9 hrs.' heating, and 4 mols. after 12 hrs.' heating. At a higher temp., a black mass is formed. He also prepared crystals of **hexapotassium nickel octohydrotetrahypophosphate,** $3K_2H_2P_2O_6.NiH_2P_2O_6.15H_2O$, by a method like that employed for the corresponding cobalt salt. The salt loses water when kept over sulphuric acid; all the water of crystallization is expelled at 100°, and the mass becomes yellow—some oxidation also occurs. P. Drawe reported six-sided, hexagonal plates of normal **sodium nickel dihypophosphate,** $Na_4P_2O_6.Ni_2P_2O_6.24H_2O$, to be formed by mixing a dil. soln. of nickel sulphate with an excess of a soln. of normal sodium hypophosphate at 0°. The formula is based on C. Bansa's analysis of the substance prepared by adding sodium acetate to the filtrate obtained from a mixed soln. of nickel sulphate and potassium dihydrohypophosphate.

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§ 23. Phosphorus Pentoxide, or Phosphoric Oxide

In 1681, Robert Boyle[1] discovered that when phosphorus is burnt in air or oxygen, white clouds are formed which condense as a voluminous white powder, which was later on termed *fleurs de phosphore*—flowers of phosphorus—by A. S. Marggraf. Observations were also made by J. C. Sturm, S. A. Frobenius, and A. G. Hanckewitz. Analyses by P. L. Dulong, and H. Davy made it clear that flowers of phosphorus is an oxide of that element. These analyses, together with those by A. L. Lavoisier, J. J. Berzelius, T. Thomson, L. J. Thénard, and A. Schrötter, showed that the composition is 43·86 per cent. of phosphorus and 56·32 per cent. of oxygen. The compound is therefore *phosphorus pentoxide*, for the simplest empirical formula is P_2O_5; it is also called *phosphoric oxide*, or *phosphoric anhydride*. The last term is employed because this oxide forms phosphoric acid when treated with water. A. L. Lavoisier knew in 1777 that phosphorus unites with oxygen in different proportions, and G. B. Sage described the preparation of white flakes of a solid by the action of dry air on phosphorus at a low temperature. The product obtained by G. B. le Sage by the combustion of phosphorus in dry air at a low temperature was probably phosphorous oxide, P_2O_3, or a mixture of the oxide with phosphoric oxide, P_2O_5, and phosphorosic oxide.

The preparation of phosphorus pentoxide.—According to H. Davy,[2] phosphoric anhydride is produced in the rapid combustion of phosphorus in the presence of a sufficient quantity of air or oxygen gas. Rapid combustion occurs at 60°, with a yellow flame in air, and a white, dazzling, intensely hot flame in oxygen. Part of the phosphoric oxide rises as a white cloud, which is luminous in the dark, and part remains as a glassy or vitreous mass where the phosphorus burns. The residue usually contains some of the lower oxides. H. Davy, for example, found phosphorus oxide, P_4O_6. As previously indicated, R. Cowper and V. B. Lewes prepared the pentoxide by passing dry air over molten phosphorus, and they noted that, under these conditions, a mixture of phosphorous oxide and crystallized phosphorus remains, and in light the latter passes into the red modification. P. Hautefeuille and A. Perrey found that in this experiment, the crystalline form of phosphoric oxide is deposited on the colder part of the tube, a vitreous variety in the hottest part, and a pulverulent form in between. The vitreous form is said to be obtained by heating either of the other two forms to dull redness; and T. E. Thorpe and A. E. H. Tutton have shown that probably P. Hautefeuille and A. Perrey's crystals were really phosphorus tetroxide, P_2O_4, and that any chemical differences are due to the presence of phosphorous oxide, P_4O_6. The other substances produced in burning phosphorus in air have been previously discussed. R. Threlfall recommended removing phosphorus from the pentoxide by distillation in a stream of purified oxygen over platinized asbestos. W. A. Shenstone and C. R. Beck said that the exposure of platinized asbestos to the vapour of phosphorus pentoxide is very undesirable as the asbestos absorbs the pentoxide very freely, which not only reduces the yield of the purified product, but also would soon remove the platinum from the sphere of action by enveloping it with a coat of the fusible products of the action. They also tried platinized porcelain, but found platinum sponge gave the best results. Roasting the pentoxide in oxygen does not remove the last traces of the lower oxides even if continued for weeks at a temp. not far below the m.p. of the pentoxide. G. I. Finch and co-workers distilled the phosphorus pentoxide in a current of oxygen flowing in a red-hot iron tube. A modification of the process has been described by H. Whitaker. According to W. A. Shenstone and C. R. Beck, phosphorus pentoxide purified by distillation in a current of oxygen is crystalline, but becomes amorphous when suddenly heated. The lower oxides impart a slight garlic-like smell to the product. Phosphorus pentoxide containing these impurities reduces a 10 per cent. soln. of silver nitrate; a boiling soln. of mercuric chloride is also reduced; and on evaporating an aq. soln., there is a faint smell of phosphine and of phosphorus tetroxide. These effects are attributed to the presence of traces of phosphorus tetroxide, P_2O_4, and phosphorous oxide, P_4O_6. E. Jungfleisch said that if dry oxygen acts on dry phosphorus below 18 mm. press., phosphorous oxide, P_2O_3, is formed; and in the cold at ordinary press., phosphoric oxide, P_2O_5, is exclusively formed.

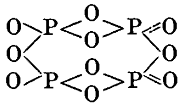
Many different methods for applying the combustion process for the preparation of the pentoxide on a large scale have been devised by J. J. Berzelius,[3] Z. Delalande, R. F. Marchand, A. G. Grabowsky, G. Pistor, T. Goldschmidt, Federal Phosphorus Co., etc. A current of dry air can be aspirated through a large glass balloon, or sheet-iron chamber, while phosphorus is burning in a porcelain dish suspended in the middle of the balloon. Fresh phosphorus is added from time to time through a suitable opening in the upper part of the combustion chamber. The exit tube leads into a wide-mouthed bottle. When sufficient of the product has collected, the bottle is closed by a well-fitting stopper, and replaced by another. A. Schrötter recommended the use of red phosphorus in the combustion process. For the condensation of the "mist" of phosphorus pentoxide, E. Britzke recommended bringing the "mist," in admixture with a large proportion of an inert gas, into intimate contact with active charcoal. As usually prepared by the combustion process, phosphorus pentoxide is a bulky, amorphous powder, but R. Threlfall showed that it can be obtained as a brittle, crystalline mass if condensed at 125°–190°. J. J. Manley removed phosphorous oxide by treatment with ozone.

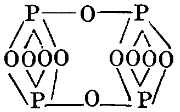
H. Davy,[4] and J. Dalton also found that phosphorus burns vigorously to the pentoxide when it is heated in the vapour of sulphur trioxide, chlorine monoxide, chlorine dioxide, nitrous and nitric oxide, and in nitrogen tri- and per-oxides. He also obtained it by heating phosphorus with conc. sulphuric acid, hypochlorous acid, and chlorous acid and nitric acid. R. F. Marchand found the same oxide is formed by the vigorous and brilliant combustion of phosphorus in molten ammonium nitrate. Phosphorus pentoxide is the end-product of the oxidation when the lower oxides are heated in air—*e.g.* phosphorous oxide (H. Davy), and phosphorus tetritoxide (A. Michaelis and M. Pitsch). The last-named also found that the tritoxide passes into the pentoxide when heated in an indifferent gas: $5P_4O=18P+P_2O_5$. A. Geuther and A. Michaelis obtained phosphorus pentoxide mixed with other products—hydrophosphoryl tetrachloride, phosphoryl chloride, nitrosyl chloride, nitrogen, and a little nitric oxide—as a by-product, during the action of nitrogen trioxide on phosphorus trichloride; and in the distillation of pyrophosphoryl chloride: $P_2O_3Cl_4=POCl_3+PO_2Cl$; and $3PO_2Cl=POCl_3+P_2O_5$; A. Besson made it by the action of a conc. soln. of phosphorous acid on an excess of phosphorus trichloride; G. Oddo, by the action of phosphoryl chloride on potassium chlorate: $2POCl_3+KClO_3=P_2O_5+KCl+3Cl_2$; and C. Mantrand, by heating bone-ash with charcoal in a current of chlorine.

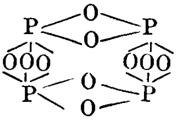
F. S. Brown and C. R. Bury [5] obtained **colloidal solutions** of phosphorus pentoxide in nitrobenzene by stirring the mixture in the presence of alcohols or organic acids. The hydroxy-compound is absorbed and peptizes the pentoxide. Traces of moisture cause coagulation. Conc. soln. set to gels on keeping.

The physical properties of phosphorus pentoxide.—Phosphorus pentoxide is a snow-white pulverulent solid. As indicated above, there are also vitreous and crystalline forms. According to H. Davy,[6] phosphorus pentoxide melts at a red-heat, and sublimes at a higher temp. E. Lautemann sublimed it in a test-tube over a spirit-lamp; and A. Schuller obtained well-defined, water-clear crystals by heating the pentoxide to 50° at one end of a tube cooled by a freezing mixture at the opposite end. The pentoxide can be melted if it be heated quickly. P. Hautefeuille and A. Perrey say that when commercial phosphoric oxide is kept many hours at 150° no other sign of sublimation occurs than a slight deposit in the cold part of the tube; sublimation appears to begin at 210° and is quite fast at 250°, but slower at lower temp. The red portions in the mass of subliming phosphorus pentoxide are supposed by H. Biltz to be the suboxide. The vitreous variety sublimes at a red-heat. R. Kempf found a crystalline sublimate is formed between 180° and 250°; and at 250°, 7·5 grms. sublimed in an hour in vacuo, and 0·38 grm. when the press. was 11 mm. According to A. Grabowsky, T. E. Thorpe and A. E. H. Tutton, and W. A. Tilden and R. E. Barnett, the volatile crystalline form is transformed into the less volatile vitreous form at about 440°. P. Hautefeuille and A. Perrey found the **vapour pressure** of phosphorus pentoxide at 250° to be 760 mm.; and they say that at a temp. a little higher, the crystals polymerize, and the vap. press. falls to a few mm. A. Smits and A. J. Rutgers showed that the vap. press. depends on the velocity of distillation; thus the vap. press. of two different samples were 1·8 atm. and 2·05 atm. at 370. They consider crystalline phosphorus pentoxide to be complex and to contain at least two allotropic forms; it melts over a large range of temp. There is transition point at 400° when the metastable sublimate changes into another form, and the transformation is accompanied by a fall of about 4 atm. in the vap. press. The volatility of the transformed pentoxide is small. The transformed solid has a m.p. of 563° at 0·59 atm. J. M. A. Hoeflake and F. E. C. Scheffer found that the usual crystalline variety has a sublimation point near 360°; between 400° and 500°, the metastable sublimate becomes amorphous and the vap. press. becomes almost zero. The amorphous form becomes a viscid liquid if heated still more and no discontinuity in the vap. press. curve appears.

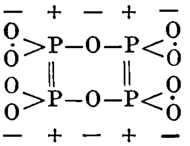
If the viscid liquid be heated a long time at 500°, it forms microscopic needles with a m.p. of 569°. There also appears to be a third form which occurs in tabular crystals, stable above 570°, but metastable in the presence of the acicular crystals. The **vapour density** determined by W. A. Tilden and R. E. Barnett at a red-heat is 336, when the calculated value for P_4O_{10} is 284; C. A. West found 300·4 at 1400° by V. Meyer's process. The simpler formula, P_2O_5, and the name phosphorus pentoxide are employed merely for convenience; actually, we are also ignorant of the mol. wt. of the solid. Several graphic formulæ can be devised for a P_4O_{10}-molecule, on the assumption that the phosphorus atoms are quinquevalent; for example, in agreement with the analyses of J. J. Berzelius,[7] A. L. Lavoiser, V. Rose, T. D. Thomson, H. Davy, P. L. Dulong, and A. Schrötter.







but there is no evidence to decide which of these, if any, is the right one. H. Henstock gave for the electronic structure:



J. Thomsen's value [8] for the **heat of formation** is $2P+5O=P_2O_5+369·9$ Cals. for the solid; and for the dissolved oxide, 405·5 Cals. H. Giran obtained with yellow phosphorus, 369·4 Cals.; with red phosphorus, 362·0 Cals.; and with red phosphorus, 360·0 Cals. Other determinations have been made by M. Berthelot, T. Andrews, J. J. B. Abria, and P. A. Favre and J. T. Silbermann. J. C. Thomlinson argued from the thermochemical data that phosphorus is quadrivalent. The **heat of solution** of the crystalline variety was found by P. Hautefeuille and A. Perrey to be 44·58 Cals.; and 41·32 Cals. for the pulverulent variety; and H. Giran found for the variety obtained by combustion, 34·37 Cals.; for the crystallized variety, 40·79 Cals.; for the amorphous variety, 33·81 Cals.; for the vitreous or glassy variety, 29·09 Cals. P. Hautefeuille and A. Perrey give 3·26 Cals. for the **heat of transformation** of the crystalline into the amorphous variety.

H. Ebert and B. Hoffmann [9] say that strongly illuminated phosphorus pentoxide gives an intense green phosphorescence. The impurities in the commercial product are not the cause of the luminescence; true, there is a pale glow due to the oxidation of the lower oxides present as impurities, but the effect with the highly purified oxide lacks only the oxidation glow. The phosphorescence also occurs in vacuo, and in different dry gases—nitrogen, coal gas, carbon dioxide, carbon monoxide, hydrogen, and helium. The exciting rays are more refrangible than the induced rays. The phosphorescence is intensified by lowering the temp. and the effect is quite brilliant at −180°. W. N. Hartley says that in the oxy-hydrogen blowpipe flame, phosphorus pentoxide gives a continuous **spectrum** with a peculiar line which also occurs in the spectrum of arsenic. H. Ebert and B. Hoffmann say the continuous spectrum has its maximum intensity in the green, and that the pentoxide exhibits a strong **phosphorescence** after illumination, especially at a low temp. F. Zecchini deduced 27·07 for the **molecular refraction** of phosphoric oxide with the μ-formula, and 17·66 with the μ^2-formula—calculated from the value for the salts; and respectively 30·24 and 17·77, from the value for metaphosphoric acid; respectively 34·59 and 19·50 from its value for pyrophosphoric acid; and respectively 29·90 and 17·37 from the value for orthophosphoric acid.

O. W. Richardson found that in the proximity of moist phosphorus pentoxide, a platinum plate charged positively to 80 volts, and at 500°–700°, is discharged, while a cold platinum plate in the vapour of phosphorus pentoxide acquires an electric charge, which it loses in time. Highly purified phosphorus pentoxide does not show the effect.

The chemical properties of phosphorus pentoxide.—E. Rutherford and F. Soddy[10] observed that radium emanation, **niton,** has no action on phosphorus pentoxide. T. E. Thorpe and A. E. H. Tutton found that commercial phosphoric oxide slowly acquires a yellow colour on exposure to light, and it becomes red in direct sunlight. Phosphorus pentoxide is extremely hygroscopic, and it dissolves in water with a hissing sound as if it were a red-hot powder; it absorbs moisture from the air very quickly, hence its use for drying gases—*vide* **hydrogen, 1.** 7, 2. P. Neogi and B. B. Adhicary observed that phosphine is produced when hydrogen is passed over a mixture of phosphorus pentoxide and reduced nickel at a dull red-heat. The affinity of phosphoric oxide for **water** is so great that it can withdraw the elements of water from many organic and inorganic substances—*e.g.* it converts nitric acid to nitrogen pentoxide, N_2O_5; it converts alcohol into ethylene, C_2H_4; sulphuric acid to sulphur trioxide, SO_3; etc. P. Hautefeuille and A. Perrey found that the crystallized oxide dissolves very rapidly in water, forming a clear soln., the pulverulent oxide forms transparent gelatinous clots which dissolve more slowly; the vitreous oxide dissolves but slowly in water. According to H. Biltz, no trace of red phosphorus or of a phosphorus suboxide is produced when phosphoric oxide deliquesces, or when it is dissolved in much water, yet there is a distinct smell of phosphorus when water is gradually added to the ordinary oxide, but not to the highly purified oxide. H. Biltz believes that phosphorus tetritoxide is formed by passing water-vapour over phosphorus pentoxide; he said that he obtained 6 mgrms. of the tetritoxide from 10 grms. of the pentoxide, and that the hot water decomposes a part of the tetritoxide to form phosphine, PH_3. The soln. of phosphoric oxide in water is phosphoric acid (*q.v.*). E. B. R. Prideaux found that with an excess of water at room temp., about 75 per cent. of the dissolved oxide is in the form of metaphosphoric acid, HPO_3, and the remainder as orthophosphoric acid, H_3PO_4. No pyrophosphoric acid, $H_4P_2O_7$, was observed. The soln. reddens blue litmus—*vide infra,* phosphoric acid. Dry phosphorus pentoxide has no action on dry litmus paper.

H. Moissan[11] found that cold phosphorus pentoxide does not react with **fluorine,** but at a dark red-heat, a flame is produced and phosphorus pentafluoride and oxyfluoride are formed. According to G. Gore, phosphorus pentoxide unites vigorously with dry **hydrogen fluoride,** forming, below 19·5°, phosphoryl fluoride, POF_3, so that the oxide cannot be used as a desiccating agent for hydrogen fluoride. G. H. Bailey and G. J. Fowler also showed that dry **hydrogen chloride** is slowly absorbed by phosphorus pentoxide, and the absorbed gas is not all given off when the product is placed in vacuo. When phosphorus pentoxide is saturated with dry hydrogen chloride, it becomes liquid, and the liquid, on distillation, gives off phosphoryl chloride, $POCl_3$, and leaves a residue of metaphosphoric acid, HPO_3. **Hydrogen bromide** behaves in a similar manner; but **hydrogen iodide** is not absorbed. Phosphorus pentoxide reacts with **sulphuric acid,** furnishing sulphur trioxide; and R. Weber found that **sulphur trioxide** unites with the phosphoric oxide, forming $P_2O_5.3SO_3$—*vide infra,* phosphoryl sulphate. H. Prinz observed no reaction with **sulphur monochloride,** S_2Cl_2, at 230°.

There is no reaction between phosphoric oxide and **nitrogen.** Phosphorus pentoxide reacts with **nitric acid,** forming nitrogen pentoxide (*q.v.*). The reaction was studied by R. Weber,[12] and J. Giersbach and A. Kessler showed that the reaction is violent only when the nitric acid contains a considerable proportion of water. H. Biltz noticed that commercial phosphorus pentoxide reacts vigorously with **ammonia,** and, with stronger heating, forms reddish-brown flecks of red phosphorus or phosphorus tetritoxide, and phosphamic acid, $P_2O_3(OH)_2$. H. Biltz found that phosphorus pentoxide which has been distilled with oxygen over spongy platinum does not show these reactions. H. Schiff found that with ammonia, amidophosphoric acid (*q.v.*) is formed; and at 0°, A. Mente found imidodiphosphoric acid (*q.v.*) is produced. G. Gustavson heated a mixture of phosphorus pentoxide and **phosphoryl chloride** in a sealed-tube at 200°, and obtained a product which he regarded as phosphorus dioxychloride, PO_2Cl, by the reaction: $P_2O_5+POCl_3=3PO_2Cl$, but G. N. Huntly distilled off the excess of phosphoryl chloride, and obtained a residue which had the empirical composition, $P_2O_5.POCl_3$, and from which carbon disulphide extracted a substance with the empirical composition, $P_2O_3Cl_4$, and left a residue, $P_7O_{13}Cl_5$. E. Berger also found that **phosphorus pentabromide** gives the phosphoryl bromide: $3PBr_5+P_2O_5=5POBr_3$. F. E. Brown and J. E. Snyder said that **vanadium oxytrichloride** is without action on phosphorus pentoxide. G. Gustavson found **boron trichloride** under similar conditions gave $P_2O_5+2BCl_3=POCl_3.BCl_3+PBO_4$, the latter may be a compound, $P_2O_5.B_2O_3$. The latter product is also formed when phosphorus pentoxide and **boric acid** are heated together. P. Hautefeuille and J. Margottet prepared the product $P_2O_5.SiO_2.4H_2O$ by heating **silica** with phosphoric acid; they have also described corresponding compounds with **titanium, zirconium, and stannic oxides.** O. Nielson studied the reaction with silica (*q.v.*).

When heated with **carbon,** H. Davy noted that phosphoric oxide is decomposed with the evolution of phosphorus and carbon monoxide. G. Gustavson heated phosphorus pentoxide with **carbon tetrachloride** in a sealed tube at 200°–300° for 48 hrs., and obtained: $P_2O_5+2CCl_4=COCl_2+CO_2+2POCl_3$; and with a smaller proportion of the carbon tetrachloride: $2P_2O_5+3CCl_4=4POCl_3+3CO_2$. The dehydrating action of phosphorus pentoxide on numerous organic compounds has been investigated; thus, H. Gal and A. Étard [13] examined its action on **acetic and benzoic acids**; L. Vanino and L. Seemann, on **formaldehyde**; F. S. Kipping, on **fatty acids**; B. Maikopar, on **phenol**; H. Biltz, on **aniline**; R. Lespieau, on **dibromopropane.** M. A. Rakusin and A. A. Arsenéeff found that phosphorus pentoxide readily dissolves to the extent of 60 per cent. in **ethyl and methyl alcohols** with the development of heat. Considerably greater quantities of the oxide dissolve in the resulting liquids, on continued stirring and heating, up to 295 g. in the case of methyl alcohol, giving a liquid of sp. gr. 1·5437 at 15 and up to 258 g. in the case of ethyl alcohol, giving a liquid of sp. gr. 1·5894 at 15°. These liquids react acid and do not boil on adding water, or give a precipitate with silver nitrate soln. H. Meerwein observed no formation of complex alkali salts by phosphorus alkoxide. W. Balareff studied the dynamics of the catalytic decomposition of ethyl alcohol by phosphorus pentoxide. Phosphorus pentoxide causes **phenol, menthol,** and similar substances to dissolve in **chloroform** without apparently entering into any reaction with them. If the soln. are left for several days and the chloroform is then removed by a current of dry air, the phosphoric oxide and the phenol are recovered unchanged.

L. Kahlenberg and W. J. Trautmann [14] observed no reaction when the pentoxide is heated with **silicon.** H. Davy found that when phosphorus pentoxide is warmed with **potassium** or **sodium,** the mixture becomes incandescent, forming the metal phosphide and phosphate; similarly with **zinc, iron,** etc., at a red-heat. H. Moissan said that it is reduced by **calcium** with explosion below redness; and by **columbium** at a red-heat. E. Solvay and M. Lucion observed a vigorous reaction between the pentoxide and **sodium oxide,** or **calcium oxide.** According to W. Odling, salts of the volatile acid anhydrides are decomposed when heated with phosphoric oxide forming phosphates and the volatile anhydride. T. E. Thorpe and F. J. Hambly found that when phosphorus pentoxide is heated with **cryolite,** phosphorus oxyfluoride, POF_3, is formed; H. Kolbe and E. Lautemann found with **sodium chloride,** phosphorus oxyfluoride, $POCl_3$, is formed; with **iodides,** C. F. Schönbein reported a turbulent reaction and the evolution of iodine; and with **selenites,** J. J. Berzelius found that selenium dioxide is given off.

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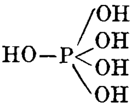
§ 24. Orthophosphoric Acid

> No substance offers the chemist greater difficulties than phosphoric acid; the more the behaviour of the acid is studied, the more the difficulties increase. Every new investigation presents the chemist with new anomalies; fresh and puzzling phenomena make their appearance, whilst the older and already known difficulties are by no means cleared up.—H. Rose.

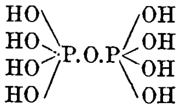
R. Boyle[1] was the first to prepare phosphoric acid. This he did by showing that the action of water on the products of combustion of phosphorus furnishes a liquid with acid properties. G. Homberg obtained similar results. F. Hoffmann supposed phosphoric acid to be a compound of vitriolic and hydrochloric acids; and G. E. Stahl, and J. Hellot argued that phosphoric acid is a compound of phlogiston with hydrochloric acid, apparently because urine contains much sodium chloride, and phosphoric acid can be extracted from urine. H. Boerhaave regarded phosphoric acid as a substance similar to sulphuric acid; and a year later, A. G. Hanckewitz, in a paper before the Royal Society, could not decide whether phosphorus is or is not a compound of sulphur. Like R. Boyle, A. S. Marggraf prepared phosphoric acid by dissolving *fleurs de phosphore* in water, and extracted it from the salts contained in urine. A. S. Marggraf also described the physical and chemical properties of phosphoric acid. As indicated in connection with the history of phosphorus, C. W. Scheele or J. G. Gann, or both, extracted the acid from bones; and in the same year, A. L. Lavoisier showed that phosphoric anhydride is a compound of phosphorus and oxygen, and established the elementary nature of phosphorus. A. L. Lavoisier prepared phosphoric acid by the action of nitric acid on phosphorus.

It was once thought that phosphoric acid existed in three isomeric forms: (i) The ordinary acid prepared by R. Boyle, and S. A. Marggraf. The sodium salt of this acid gives a yellow precipitate with silver nitrate, and the liquid possessed an acid reaction. (ii) A salt of an acid was prepared by T. Clark in 1827 by heating the ordinary phosphate. The sodium salt of this acid gives a white precipitate with silver nitrate, and the liquid remains neutral. (iii) The acid obtained by J. J. Berzelius, by a thorough calcination of phosphoric acid. This acid also gives a white precipitate with silver nitrate, and, unlike the other two forms, coagulated a clear aq. soln. of albumen. It was known that the sodium salts of ordinary and of T. Clark's phosphoric acid crystallized from aq. soln. with different amounts of water, but no importance was attached to this fact because it was regarded simply as water of crystallization. F. Stromeyer, and others supposed the two acids to be isomeric modifications. J. L. Gay Lussac made a special study of the salts of T. Clark's acid. In 1833, T. Graham showed that the water of the acids should not be disregarded as an accidental feature because the water plays an essential part in the formation of the acid where it assumes the function of a base. Thomas Graham proved that all three acids—which he called respectively ordinary, pyro-, and metaphosphoric acids—were different modifications of phosphoric acid; and that they differed from one another by "the quantity of water combined with the acid." In orthophosphoric acid, the water and anhydride are united in the proportion $3H_2O : P_2O_5$; in pyrophosphoric acid, $2H_2O : P_2O_5$; and in metaphosphoric acid, $H_2O.P_2O_5$. T. Graham also found that when the acids were saturated with a base, three series of phosphates were obtained, one series contained one equivalent of the base per equivalent of the anhydride—*primary phosphates;* a second series contained two equivalents of the base—*secondary phosphates;* and a third series contained three equivalents of the base—*tertiary phosphates.*

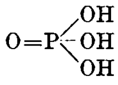
The relation of the three phosphoric acids to phosphoric oxide, P_2O_5, will be evident from the following scheme, where phosphorus is assumed to be quinquevalent:



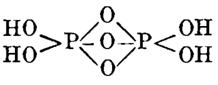
H_5PO_5, or
$P_2O_5.5H_2O$



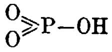
$H_8P_2O_9$, or
$P_2O_5.4H_2O$



H_3PO_4, or
$P_2O_5.3H_2O$



$H_4P_2O_7$, or
$P_2O_5.2H_2O$



HPO_3, or
$P_2O_5.H_2O$

The first two are unknown, the third is ordinary orthophosphoric acid, the fourth pyrophosphoric acid, and the last metaphosphoric acid. I. Fröschl[2] accounted for the different behaviour of the five hydroxyl groups in phosphoric acid by assuming that in the strictly orthophosphoric acid, $P(OH)_5$, three have an acidic character, one is amphoteric, and one is basic. Hence, complex salts should be possible, and he prepared **sodium carbonatophosphate,** $Na_2H_3(CO_3)(PO_4)$; **potassium disulphatophosphate,** $2K_2SO_4.H_3PO_4$; **potassium sulphatophosphate,** $K_2SO_4.H_3PO_4$; **ammonium sulphatophosphate,** $(NH_4)_2SO_4.(NH_4)H_2PO_4$. The minerals apatite, wagnerite, and dahllite are supposed to belong to the same class of salts, and also the fluophosphates described by R. F. Weinland and J. Alfa. P. Lemoult reported a number of derivatives of pentabasic phosphoric acid, $P(OH)_5$, of the type $P(OH)(NH.R)_4$. It will be observed that by keeping consistently to the notation employed for periodic acid, and several other acids, the unknown $P(OH)_5$ should be *orthophosphoric acid,* but this term has got into use for the $PO(OH)_3$-acid, which ought to be called *paraphosphoric acid,* $PO_2(OH)$; and **metaphosphoric acid** would retain its present designation. Similarly, $(HO)_4P.O.P(OH)_4$ would be called *orthodiphosphoric acid,* or *orthopyrophosphoric acid.* Hemihydrated phosphoric acid may be regarded as *orthodiphosphoric acid;* and the mineral libethenite as the calcium salt—*vide infra.* The next dehydration product, $(HO)_3P{=}O_2{=}P(OH)_3$, would be *paradiphosphoric acid* or *diparaphosphoric acid,* $(H_3PO_4)_2$; while $(HO)_2P{\equiv}O_3{\equiv}P(OH)_2$, at present called *pyrophosphoric acid* or *diphosphoric acid,* becomes *mesodiphosphoric acid*; $(HO)P{\equiv}O_4{\equiv}P(OH)$ is the ordinary *metadiphosphoric acid—vide infra.*

Orthophosphoric acid or salt of the acid was formed by A. J. Balard,[3] E. Soubeiran, T. J. Pelouze, M. Bengeiser, A. R. Leeds, etc., by passing phosphorus vapour over red-hot alkali carbonate, or by the action of an oxidizing agent; sulphur trioxide or sulphuric acid; nitrous or nitric oxide; nitrogen peroxide; or nitric acid. It is also formed by the action of phosphorus on an iodate, periodate, bromate, chlorate, perchlorate, nitrate, or metal oxide whereby a mixture of metal phosphate and phosphide is formed. Some of these reactions are dangerously explosive. Phosphoric acid can be made by boiling an aq. soln. of the products of combustion of phosphorus with nitric acid so as to oxidize the lower oxides, and to transform the meta- into orthophosphoric acid. Meta- and pyrophosphoric acids can be hydrated to the ortho-acid by the action of heat in the presence of strong acids. The acids of the lower oxides—H_3PO_2, H_2PO_3, and $H_4P_2O_6$—can be oxidized to orthophosphoric acid. Thus, A. Michaelis and M. Pitsch oxidized the tetritoxide by iodine, sodium hypochlorite, or sulphuric acid; H. Rose oxidized hypophosphorous acid by heating it in air, and by the action of hypochlorous or nitric acid; P. L. Dulong used iodine or chlorine, and also soln. of mercury, silver, or gold salts. C. A. Wurtz oxidized phosphorous acid by prolonged exposure to air or by treatment with conc. sulphuric acid; H. Davy used chlorine, hypochlorous acid, iodic acid, nitric acid, and salts of mercury, gold, silver, etc. A. Cavazzi oxidized phosphine by treatment with sulphur acid at 60° or 70°; H. Rose used conc. sulphuric acid at ordinary temp.; and P. Thénard, chlorine-water. C. F. Bucholz boiled B. Pelletier's acid with nitric acid. A. Sommer recommended oxidation with bromine when hydrobromic acid is obtained as a by-product. M. Pettenkofer also recommended making phosphoric acid by boiling with nitric acid the by-product obtained in the preparation of hydriodic acid from iodine, phosphorus, and water. F. G. Liljenroth made the acid by the action of hot water or steam on phosphides with or without a catalyst; and E. Urbain recovered the phosphorus evolved in the preparation of activated carbon, in the form of phosphoric acid by a modification of this process.

A great many chemists—M. Martres, etc.—have described the preparation of phosphoric acid by the action of boiling nitric acid on phosphorus. The method was employed by A. L. Lavoisier in 1780, and strongly recommended by T. Bergman, who said: "Nothing but a prudent management of the fire is required to procure the acid with the greatest ease in a state of as great purity as by the tedious and wasteful method of combustion in air." Phosphorus is scarcely attacked even by 6 months' contact with cold dilute nitric acid of sp. gr. 1·012, but with more concentrated acid, the action is more marked. Some ammonia is formed during the reaction, and the amount reaches a maximum with nitric acid of sp. gr. 1·18.

Orthophosphoric acid is conveniently prepared by boiling one part of red phosphorus with 16 parts of nitric acid—sp. gr. between 1·20 and 1·25—in a flask fitted with a reflux condenser and a ground glass-joint at the neck. Any nitric acid which is volatilized will thus be returned to the flask. Yellow phosphorus is not so quickly attacked by nitric acid as red phosphorus, possibly because the former melts and forms masses which do not present so nearly as large a surface to the action of the acid as do the particles of red phosphorus. The latter is more expensive. When the phosphorus is all oxidized, the soln. is evaporated to dryness, and the residue is finally heated in a platinum dish to a temp. not exceeding 180° to make sure that all the nitric acid is driven off. The boiling liquid usually shows the presence of phosphorous acid, which is subsequently oxidized to phosphoric acid. Whether the primary action results in the formation of both acids or of phosphorous acid alone is not clear. If the acid employed for the oxidation be more conc. than that just indicated an explosion may ensue; and if a weaker acid be used the action is very slow.

M. Pettenkofer, W. J. Horn, and G. A. Ziegeler showed that the presence of a trace of iodine will accelerate the reaction, which then runs more smoothly. G. A. Ziegeler recommends 0·3 to 0·6 grm. of iodine per 100 grms. of phosphorus. P. Wagner, and G. F. H. Markoe noted that bromine acts in a similar way. The nitric acid should be free from sulphuric acid.

If the phosphorus contains arsenic, the phosphoric acid will be contaminated with arsenic acid. W. T. Wenzell, E. W. Runyon, L. A. Buchner, G. Watson, J. von Liebig, C. F. Bärwald, etc., have described processes for eliminating the arsenic. In these, the aq. soln. of the acid is sat. with hydrogen sulphide, and allowed to stand some days in a closed flask; renewal of the hydrogen sulphide is necessary from time to time. The filtered liquid is freed from hydrogen sulphide by evaporation. W. Gregory purified phosphoric acid by heating it between 320° and 350° so as to transform it into metaphosphoric acid, and the impurities into insoluble metaphosphates. The metaphosphoric acid is leached out by water, and transformed into orthophosphoric acid as indicated above. The process of purification—J. B. Trommsdorff, G. Watson, H. W. F. Wackenroder, etc.—by precipitating the impurities with alcohol is too expensive. A. J. Balard, and P. L. Dulong precipitated the calcium phosphate (and magnesium phosphate) with ammonium carbonate. According to R. Maddrell, the acid purified by W. Gregory's process still retains magnesium and sodium phosphates. In J. N. Carothers and A. B. Gerber's process, conc. phosphoric acid is partially freed from arsenic, lead, lime, and fluorine by chemical methods, and is then subjected to a current of air at a temperature of 50° to remove volatile impurities. The suspended solids are then separated and the acid cooled, when crystalline phosphoric acid separates. B. Laporte treated sodium phosphate with barium sulphide, etc.: $3BaS + 2NaOH + 2Na_2HPO_4 = Ba_3(PO_4)_2 + 3Na_2S + 2H_2O$; and the washed barium phosphate is treated with sulphuric acid, etc.

Phosphoric acid is not usually prepared in the laboratory because an acid of a high degree of purity can be readily obtained in commerce. Only in special cases is the preparation conducted in the laboratory. The hydrolysis of the phosphoric or phosphoryl halides—PF_5, POF_3, PCl_5, $POCl_3$, PBr_5, and $POBr_3$—furnishes fairly pure phosphoric acid, $PCl_5 + 4H_2O = H_3PO_4 + 5HCl$, when the volatile acid has been removed by evaporation in a platinum dish. A. Geuther and A. Michaelis found that phosphoric acid is likewise produced by the action of pyrophosphoryl chloride on water. H. E. W. Phillips prepared the acid in the following manner:

> Phosphorus trichloride twice redistilled was mixed very slowly with specially purified water, the flat porcelain dish in which the addition was made being floated on cold water during the operation. It was found that, if the addition was made too rapidly, a discoloration was produced, which at the end of the preparation was seen to be due to a fine powder suspended in the liquid. The phosphorous acid was then heated until it gave no precipitate with silver nitrate. It was then oxidized by cautious addition of dil. nitric acid, when an active effervescence ensued. Nitric acid was eventually added in slight excess, and the evaporation continued until all the nitric acid was expelled. The phosphoric acid thus prepared was transparent and colourless. The 100 per cent. acid did not affect litmus paper, and had no action on sodium carbonate.

A. Joly[4] recommended treating purified ammonium phosphate with boiling conc. hydrochloric acid. The liquid was separated from the precipitated ammonium chloride, and heated with nitric acid to drive off the ammonia and hydrochloric acid. The nitric acid is expelled by evaporating the soln. as indicated above. A. Ditte, and G. Watson used sodium phosphate and conc. hydrochloric acid; M. Nicolas, calcium phosphate or natural phosphates and hydrofluoric acid; A. Gutensohn heated aluminium phosphate with tin shavings in an iron vessel; H. N. Warren electrolyzed a soln. of copper phosphate in dil. phosphoric acid; J. J. Berzelius prepared lead phosphate by adding a soln. of lead acetate to a nitric acid soln. of bone-ash, and decomposed the lead phosphate by treatment with dil. sulphuric acid, and removed the last traces of lead by hydrogen sulphide; and W. Odling treated a soln. of sodium phosphate in ice-cold water with lead acetate, and decomposed the washed precipitate suspended in water with hydrogen sulphide. The soln., freed from the precipitated lead sulphide, was evaporated to remove the hydrogen sulphide. J. Persoz digested the soln. of bone-ash with ferric or aluminium oxide, decomposed the precipitated phosphate with sulphuric acid, and afterwards extracted with phosphoric acid with alcohol. L. Thompson precipitated the lime by treating the calcium phosphate with oxalic acid. W. H. Ross and co-workers purified phosphoric acid by a process of fractional crystallization.

Industrially, phosphoric acid has been prepared from bone-ash, from natural phosphates, or from Thomas-slag. Many processes have been suggested,[5] and patent specifications filed,—*e.g.* by A. Adair and W. Thomlinson, H. and E. Albert, A. J. Balard, L. Blum, M. Brandon, A. Colson, G. Deumelandt, A. Drevermann, P. Dietrich, E. Dreyfus, P. L. Dulong, J. M. J. Funke, W. Gregory, R. Hasenclever, M. Hatmaker, J. Meckstroth, A. House, L. Carpenter, R. Suchy, A. Aita, H. G. C. Fairweather, W. G. Waldo, E. W. Guernsey and J. Y. Yee, J. N. Carothers, K. D. Jacob, L. Imperatori, G. Leuchs, J. von Liebig, T. Lomax, R. Maddrell, H. Merz, T. Meyer, J. Neustadl, N. B. Powter, G. Rocoeur, F. S. Washburn, A. Rose, C. Runzler, W. H. Ross and co-workers, C. Scheibler, R. Schliwa,

S. G. Thomas, S. G. Thomas and T. Twymann, J. B. Trommsdorff. In many of these the phosphate is treated with the calculated quantity of dil. sulphuric acid for precipitating the lime, and after the mixture has stood some time, it is pumped through a filter-press so as to separate the calcium sulphate precipitate from the phosphoric acid which has a sp. gr. approximating 1·07 or 1·09. The liquor is then evaporated in lead pans until its sp. gr. is nearly 1·53. If necessary, the acid can be treated with more sulphuric acid to precipitate more calcium sulphate, and the clear liquor evaporated to dryness, and ignited to drive off the excess of acid. The product is nearly free from lime and sulphuric acid, but retains magnesium phosphate. The cakes from the filter-press are used for agricultural purposes. W. H. Waggaman and co-workers, T. Swann, W. Kyber, and W. H. Ross and co-workers described the preparation of phosphoric acid from phosphatic rocks by heating at a high temp. a mixture of the natural phosphate with silica and coke, and collecting the volatilized phosphoric acid in a suitable chamber. A calcium silicate slag remains. F. J. Maywald heated the mixed phosphates by a low potential arc, and collected the volatilized phosphoric acid. The volatilized acid prepared by the volatilization process is at least of an equal degree of purity with that prepared by the sulphuric acid process.

Table III by W. H. Ross[6] and co-workers shows the amount of impurity in some commercial phosphoric acids prepared by the sulphuric acid process *S* and by the volatilization process *V* from phosphate rock *R* or bones *B*. The commercial acid may be crude *C* or refined *P*. Arsenic and lead are expressed in parts per million. The lead is largely derived from the lead containers. The presence of *phosphorous acid* as an impurity in phosphoric acid is revealed by its giving a black instead of a yellow precipitate with mercurous nitrate; a precipitate of sulphur when heated with sulphurous acid; and evolving phosphine when heated with dil. sulphuric acid. The presence of metaphosphoric acid is indicated by the white precipitate obtained by its coagulating white-of-egg.

TABLE III.—THE COMPOSITION OF SOME COMMERCIAL PHOSPHORIC ACIDS.

Phosphorous acid.	Sp. gr.	H_3PO_4 per cent.	Percentage constituents on the basis of 50 per cent. concentration.										
			Na	K	Ca	Fe	Al	Mn	Pb	As_2O_3	H_2SO_4	HCl	HF
R.S.C.	1·4606	53·47	0·20	tr.	0·14	1·21	0·66	0·216	9	2·0	0·47	0·012	0·20
R.S.C.	1·2371	27·60	0·76	0·08	1·20	1·88	1·22	0·149	0	1·0	0·65	0·027	0·54
R.V.C.	1·5428	69·99	0·13	0·04	0·04	0·18	0·27	0·004	4	1·0	0·27	0·013	0·19
R.S.P.	1·4123	55·20	0·41	0·12	tr.	0·19	0·10	0·155	7	0·75	0·46	0·044	0·05
R.S.P.	1·4221	55·12	0·35	tr.	0·16	0·34	0·23	0·348	4	1·0	0·13	0·035	0·11
R.S.P.	1·3261	39·40	0·06	0·03	0·14	1·00	1·25	0·184	14	1·0	1·25	0·012	0·96
B.S.P.	1·3805	52·27	0·16	tr.	0·20	0·50	0·11	0·014	0	2·5	0·42	0·003	0·04
B.S.P.	1·2309	32·15	0·53	tr.	1·36	0·84	0·19	0·021	9	1·0	0·28	0·023	0·14
R.V.P.	1·3955	56·89	0·10	0·16	0·00	0·08	0·04	0·005	12	1·0	0·09	0·000	0·02
R.V.P.	1·6310	79·50	0·12	0·18	tr.	0·17	0·06	0·004	8	0·05	0·07	0·000	0·01

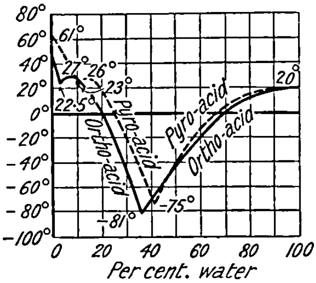


FIG. 40.—Freezing-point Curves of Water with Orthophosphoric Acid and with Pyrophosphoric Acid.

The hydrates of phosphoric acid.—J. F. H. Süersen[7] found the crystals of phosphoric acid to be easily soluble in water, and H. Giran obtained the results shown by the continuous curve, Fig. 40, for the f.p. of mixtures of orthophosphoric acid and water. There are two minima, 22·5° and —81°; the former corresponds with $H_3PO_4+0{\cdot}135H_2O$, and the other with $H_3PO_4+3{\cdot}205H_2O$, the maximum occurring with the hemihydrate. W. H. Ross and R. M. Jones gave —85° for the one eutectic temp., and 23·50° for the other. A. Smith and A. W. C. Menzies have measured the solubility of the ortho-acid in water at different temp. The results constitute a more detailed study of the f.p. curve for the more conc. soln. of orthophosphoric acid. The following numbers are selected from their data:

	−16·3°	0·5°	27°	29·35°	25·41°	24·11°	25·85°	26·23°	42·30°
Per cent. H_3PO_4 .	76·7	78·7	87·7	91·6	94·1	94·78	95·54	95·90	100
Solid phases . .	$2H_3PO_4.H_2O$					$10H_3PO_4.H_2O$		H_3PO_4	

The results are graphed in Fig. 41. *AB* is the solubility curve of A. Joly's hydrate. $2H_3PO_4.H_2O$; *B* is the melting point of this hydrate (29·35°); *BC*, the effect of phosphoric acid on the m.p. of the hemihydrate; *CD*, the solubility curve of $10H_3PO_4.H_2O$; and *C* is the eutectic point (23·5°) of the two hydrates; *D* is the transition point (26·2°); *DE* is the solubility curve of orthophosphoric acid; and *E* is the melting point (42·30°) of orthophosphoric acid. W. H. Ross and R. M. Jones observed no break in the curve at *D*, and were unable to confirm the existence of the hydrate, $10H_3PO_4.H_2O$. J. Kendall and co-workers studied the hydrate formation with this and related acids.

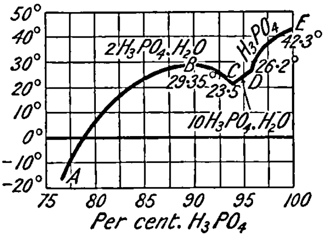


FIG. 41.—Solubility Curve of Orthophosphoric Acid.

According to A. Joly, if a conc. soln. of the approximate composition $H_3PO_4 + 0·3H_2O$ be sown with a crystal of phosphoric acid, the mother-liquid remaining after the crystallization has the composition $2H_2PO_4.H_2O$, and this solidifies to a mass of prismatic plates of **hemihydrated orthophosphoric acid,** $2H_3PO_4.H_2O$. The undercooled soln. of this hydrate crystallizes when sown with crystals of the isomorphous hemihydrated arsenic acid. A. Smith and A. W. C. Menzies have found that A. Joly's hydrate is stable between —16·3° and 25·41°. It has been suggested that the hemihydrate $2H_3PO_4.H_2O$ is really an octobasic phosphoric acid, or orthodiphosphoric acid, $H_8P_2O_9$, represented by the salts, tetracalcium phosphate, $Ca_4P_2O_9$; *libethenite,* $Cu_4P_2O_9.H_2O$, etc. Since orthophosphoric acid is probably $H_6P_2O_4$, the theoretical hydroxyl derivatives with a $\equiv P-O-P\equiv$ nucleus are:

Acid . .	$(HO)_8P_2O$	$(HO)_6P_2O_2$	$(HO)_4P_2O_3$	$(HO)_2P_2O_4$
Calcium salt	$Ca_4P_2O_9$	$Ca_3P_2O_8$	$Ca_2P_2O_7$	CaP_2O_6
	Orthopyrophosphoric acid.	Paradiphosphoric acid.	Metapyrophosphoric acid.	Metaphosphoric acid.

A. Smith and A. W. C. Menzies obtained **decitahydrated orthophosphoric acid,** $10H_3PO_4.H_2O$, stable between —24·11° and 25·85°, Fig. 41. This hydrate forms large transparent prisms which pass into anhydrous orthophosphoric acid, H_3PO_4, at 26·2°. W. H. Ross and R. M. Jones were unable to confirm these observations. P. L. Huskisson found crystals which had separated from a sample of sp. gr. 1·750 (88·8 per cent.) induced crystallization in acids of specific gravity from 1·66 (82 per cent.) to 1·75 at ordinary temp., but not so in acids of higher or lower specific gravity. The work of A. Smith and A. W. C. Menzies shows that the crystals were those of the hemihydrate, $2H_3PO_4.H_2O$, and if P. L. Huskisson had worked below 13° he would have obtained crystals from the less conc. soln. The crystals P. L. Huskisson obtained by allowing a soln. of sp. gr. 1·75 to stand in vacuo were those of H_3PO_4; and in such soln., the crystals of the hemihydrate induced no crystallization. The formation of the hydrates was discussed by J. Kendall and co-workers. Attempts by A. Sänger to prepare the *monohydrated orthophosphoric acid,* $H_3PO_4.H_2O$, *i.e.* $P(OH)_5$, were not successful, although P. Lemoult did prepare organic derivatives of pentabasic phosphoric acid, $RO.P(NH.R)_4$. H. Crompton found that the second differential of the electrical conductivity gave breaks corresponding with the hydrates $H_3PO_4.2H_2O$, and $H_3PO_4.7H_2O$, which are the same as those found by D. I. Mendeléeff from the first differential coefficient of the sp. gr. curves—*vide* sulphuric acid.

The physical properties of phosphoric acid.—J. F. H. Süersen,[8] P. A. Steinacher, and F. Stromeyer noted that spontaneous crystallization occurs if the viscid liquid be left at rest for some days. The transparent crystals are either four-sided prisms or six-sided prisms with quadrilateral summits. A. Joly said that the **crystals** belong to the rhombic system. According to G. Tammann, when the soln. of phosphoric acid has been evaporated to the point where the bubbling and spurting suddenly cease, the syrupy liquid has a composition corresponding with H_3PO_4; and, according to G. Krämer, this liquid furnishes transparent prismatic crystals on cooling. The syrupy liquid does not crystallize readily owing to surfusion. W. H. Ross and R. M. Jones saw that the rates of crystallization of the hemihydrated and anhydrous phosphoric acid are respectively 2·6 cms. and 33·3 cms. per minute at 22°. If the conc. be carried further than this, H. P. Cooper said that the liquid gelatinizes and some pyro- and meta-phosphoric acids are formed; but P. L. Huskisson stated that if the evaporation be conducted in vacuo beyond a sp. gr. 1·860, transparent plates are formed which become opaque with the development of heat on exposure to air. H. E. W. Phillips did not find the 100 per cent. acid to crystallize, except occasionally when cooled to 0°. J. Thomsen found the conc. soln. of the acid crystallizes readily if sown with some crystals of the solid acid. H. P. Cooper said that a crystal of Glauber's salt in a soln. of sp. gr. 1·850, crystallizes rapidly, but this statement is probably a *mal*-interpretation of the observed result, and is not a true case of crystallization by seeding. Crystallization occurs rapidly with the development of heat by the inoculation of a soln. of sp. gr. 1·750 with a crystal of orthophosphoric acid; with a soln. of sp. gr. 1·660, crystallization proceeds more slowly, and furnishes prismatic needles. The crystals are deliquescent. J. Dalton [9] measured the **specific gravity** of a few solutions of phosphoric acid of known composition. According to H. Schiff, the sp. gr. of the syrupy liquid of the composition H_3PO_4 is 1·88, and he represented the sp. gr., D, of a soln. with p per cent. of phosphoric acid, H_3PO_4, by the formula $D=1+0{\cdot}005378p+0{\cdot}00002886p^2+0{\cdot}00000006p^3$. Tables have been prepared by H. Watts, H. Schiff and A. Ott, etc. The results by H. Hager are indicated in Table IV. If the percentage of P_2O_5 be multiplied by 1·38, it furnishes the corresponding amount of H_3PO_4. Observations were also made by N. P. Knowlton and A. C. Mounce, D. I. Mendeléeff, W. H. Ross and R. M. Jones, W. Thörner, and F. K. Cameron and W. O. Robinson. E. Cornec measured the sp. gr. of soln. of phosphoric acid while being progressively neutralized by potassium hydroxide, and found a marked minimum corresponding with the dihydrophosphate, and a maximum corresponding with the normal

TABLE IV.—THE SPECIFIC GRAVITY OF AQUEOUS SOLUTIONS OF PHOSPHORIC ACID OF DIFFERENT CONCENTRATIONS.

Per cent. P_2O_5	Specific gravities at 17·5°.									
	0	1	2	3	4	5	6	7	8	9
0	—	1·005	1·011	1·021	1·029	1·037	1·045	0·053	1·062	1·070
1	1·079	1·087	1·096	1·104	1·113	1·122	1·130	1·140	1·150	1·159
2	1·169	1·178	1·188	1·198	1·208	1·218	1·228	1·239	1·249	1·260
3	1·271	1·281	1·292	1·303	1·314	1·325	1·336	1·348	1·359	1·371
4	1·383	1·396	1·409	1·422	1·435	1·448	1·462	1·476	1·491	1·505
5	1·521	1·536	1·551	1·566	1·581	1·597	1·613	1·629	1·645	1·661
6	1·677	1·701	1·709	1·725	1·741	1·766	1·775	1·792	1·809	—

phosphate. The **viscosity** of soln. of phosphoric acid have been measured by J. L. M. Poisseville,[10] K. T. Slotte, etc. With water unity, R. Reyher found for N-, $\frac{1}{2}N$-, $\frac{1}{4}N$-, and $\frac{1}{8}N$-soln., at 25°, respectively 1·2871, 1·1331, 1·0656, and 1·0312; and B. E. Moore, at 18°, for soln. with 0·25, 0·5, 1·0, and 2·0 mols per litre, the respective values 1·064, 1·143, 1·311, and 1·739. A. Smith and A. W. C. Menzies found no maximum in the solubility curve of mixtures of 90·6 to 98·1 per cent. of orthophosphoric acid with water. L. J. Simon measured the viscosity of phosphoric acid while being neutralized with sodium hydroxide. T. Graham found that the **rate of diffusion** of phosphoric acid is such that in eight days 9·1 grms. of the acid diffused from a soln. of 4 grains of H_3PO_4 in 100 grms. of water at 15·6°. For phosphoric acid, at 20°, L. W. Oholm gave for $3N$-, $2N$-, N-, and $0{\cdot}25N$-soln., $k=0{\cdot}644$, 0·656, 0·692, and 0·772 respectively. The **coefficients of cubical expansion** of soln. of phosphoric acid were determined by C. Forch,[11] W. Thörner, and H. Schiff. C. Forch gave:

Per cent.	0°–5°	5°–10°	10°–15°	15°–20°	20°–25°	25°–30°	30°–35°	35°–40°
4·8	48	109	164	220	266	309	352	387
17·8	188	228	267	304	337	371	399	430

The true **melting point** of orthophosphoric acid is difficult to determine on account of the depression which is produced by traces of water absorbed by the hygroscopic crystals. J. Thomsen[12] found 38·6°; W. Borodowsky, 36·6°; M. Berthelot, 41·75°; A. Smith and A. W. C. Menzies, 42·30°; and W. H. Ross and R. M. Jones, 42·35°. G. Tammann represented the effect of press. p kgrms. per sq. cm., on the m.p., θ°, of orthophosphoric acid by $\theta=38{\cdot}0+0{\cdot}00800p$, or

θ	38·3	40·93°	44·98°	49·94°	54·93°	59·98°
p	1	410	960	1500	2032	2695

H. Giran measured the f.p. curve of mixtures of orthophosphoric acid and water. His curve shows two minima, one at 22·5° and one at —81°, with one maximum at 29°, and he concluded that 29° is the m.p. of the hemihydrate. The minimum —81° is probably the cryohydric point for the mixture $H_3PO_4+0{\cdot}135H_2O$. H. Giran's m.p. of $2H_3PO_4.H_2O$, 29°, is two degrees higher than A. Joly's own value, 27°. A. Smith and A. W. C. Menzies give 29·35°; and W. H. Ross and R. M. Jones, 29·32°. Probably owing to undercooling effects, H. Giran missed the decitahydrate. For the m.p. of mixtures of phosphorous and phosphoric acids, *vide* Fig. 37. J. Kendall and co-workers, and H. C. Jones measured the mol. **lowering of the freezing point** in aq. soln., and calculated values for the degree of ionization. G. Rümelin[13] found for soln. with 15·41, 21·57, 28·21, and 32·75 per cent. H_3PO_4, the **specific heats** 0·834, 0·813, 0·776, and 0·697 respectively.

The **vapour pressures** of aq. soln. of orthophosphoric acid were measured by L. von Babo[14] in 1847; at the b.p. 122°, the vap. press. is 760 mm.; at 35°, 20 mm.; at 65°, 92 mm.; and at 78°, 164 mm. C. Dieterici found at 0° soln. with 0·945, 22·32, 124·9, and 390·2 grms. in 100 grms. of water had a vap. press. of 4·612, 4·377, 2·710, and 0·636 mm. respectively. G. Tammann measured the lowering of the vap. press. of water at 100°, and found with 20·75, 149·16, and 330·52 grms. of phosphoric acid in 100 grms. of water lowered the vap. press. respectively 30·1, 290·9, and 507·3 mm. A. Smith and A. W. C. Menzies found the vap. press. of the hydrate systems attained a state of equilibrium very slowly; a sat. soln. of the hydrate $2H_3PO_4.H_2O$ at 24·99° had a vap. press. of 0·85 mm. I. Fröschl measured the mol. wts. determined by the **elevation of the boiling point** for soln. of different conc., and the resulting curve exhibited discontinuities with 7 and 13 per cent. of H_3PO_4. For soln. with 1 to 6·5 per cent. H_3PO_4, the mol. wt. was 137·2; with soln. 7 to 12 per cent. H_3PO_4, 125·9; and with soln. 14 to 27 per cent. H_3PO_4, 115·7—the theoretical value for H_3PO_4 is 98.

J. Thomsen[15] gave —2·52 Cals. for the **heat of fusion** of orthophosphoric acid, H_3PO_4; and A. Joly, —7·28 Cals., for the heat of fusion of the hemihydrate, $2H_3PO_4.H_2O$. J. Thomsen gave for the **heat of formation** $(H_3,P,O_4)=302{\cdot}56$

Cals. for the crystalline salt, and 300·04 for the fused salt; and 305·29 Cals. for the salt in soln. H. Giran gave respectively 305·83, 303·32, and 308·53 Cals. A. Joly gave for $P_2O_5+H_2O_{solid}=P_2O_5.3H_2O+29\cdot6$ Cals.; and H. Giran, for the **heat of hydration** of solid, liquid, and soln. of pyrophosphoric acid, $H_4P_2O_7$, with liquid. water to form respectively solid, liquid, and soln. $2H_3PO_4$, 6·97, 9·09, and 4·25 Cals. respectively. A. Joly gave for $P_2O_5.3H_2O_{solid}=P_2O_5.4H_2O_{solid}$(or $2H_3PO_4.H_2O$) $+3\cdot7$ Cals., $P_2O_5+4H_2O_{solid}=P_2O_5.4H_2O+33\cdot3$ Cals. G. Rümelin gave for the **heat of dilution** of soln. with 11·19, 13·88, 19·88, and 29·99 mols of water per mol of H_3PO_4, the respective values 33·13, 19·93, 12·26, and 8·23 Cals. respectively. P. A. Favre and J. T. Silbermann gave 323·9 cals. for the **heat of neutralization** of a gram of a dil. soln. of potassium hydroxide with orthophosphoric acid, and 480·1 cals. for sodium hydroxide. J. Thomsen found the heat of neutralization of a mol of phosphoric acid with a soln. of *n* mols of sodium hydroxide: $H_3PO_{4aq.}+nNaOH_{aq.}$

n	0·5	1·0	2·0	3·0	6·0
Heat of neutralization .	7·3	14·8	27·1	34·0	35·3 Cals.

M. Berthelot and W. Longuinine obtained rather smaller values. This shows that eq. proportions of sodium hydroxide have very different thermal values—the first equivalent 14·8 Cals., the second, not very different, 12·3 Cals., and the third 6·9 Cals. R. de Forcrand found the total value of the three acid functions of phosphoric acid: $H_3PO_{4aq.}+Na_{3aq.}=H_{3gas}+Na_3PO_{4aq.}+148\cdot13$ Cals., with a mean value for each 49·38 Cals. The observed value for the first is 60·6 Cals., for the second 49·2 Cals., and for the third, 38·83 Cals. The thermal value of the first acidic hydrogen is high because of intramolecular combinations; the second is less, showing that the displacement is more easily effected once the way has been opened; and similarly with the third. M. Berthelot obtained for the heat of neutralization of $n=1$ and $n=2$ mols of ammonium hydroxide with a mol. of phosphoric acid respectively 13·5 and 26·3 Cals.; while for the hydroxides of the alkaline earths, by the dissolution of a mol. of H_3PO_4 in six litres of water at 16°, and 0·5CaO, CaO, and 1·5CaO, 14·8, 24·5, and 29·8 Cals. respectively; with strontium oxide similarly, 15·05, 25·3, and 30·3 Cals.; and with barium oxide, 15·0, 25·4, and 30·4 Cals. P. Tutoit and E. Grobet measured the temp. of the soln. during the progressive neutralization of phosphoric acid and obtained three characteristic breaks. O. Stelling studied the **X-ray spectrum.**

J. Thomsen gave for the **heat of solution** of a mol. of the crystalline acid, 2·69 Cals.; and of the liquid acid, 5·21 Cals. A. Joly gave for $P_2O_5.3H_2O_{solid}$ in 400 mols. of water at 13°, 5·34 Cals.; for $P_2O_5.4H_2O_{solid}$, 0·28 Cal.; and $P_2O_5.4H_2O_{liquid}$, 7·56 Cals.; for $P_2O_5.4H_2O+1700H_2O$, 0·62 Cal.; for $P_2O_5.4H_2O+260H_2O$, 0·16 Cal.; for $P_2O_5.4H_2O+200H_2O$, 0 Cal.; and for $P_2O_5.4H_2O+160H_2O$, —0·14 Cal. E. Petersen has measured the heat of dilution; and E. Bose, the heat of mixing. P. A. Favre and J. T. Silbermann find the thermal eq. of $H_3PO_4 : H_3PO_3 : H_3PO_2$ are related as 4·36 : 2·91 : 1. J. C. Thomlinson made some calculations on the heat of formation of the acids of phosphorus on the assumption that phosphorus is quadrivalent. S. Arrhenius gave for the **heat of ionization** per mol.: $H_3PO_4=H^{\cdot}+H_2PO'_4$ —1·82 Cals. at 35°, and —1·53 Cals. at 21·5°. The negative value of the heat of ionization is supposed to explain why the heat of neutralization exceeds 13·5 Cals., the normal value for the stronger acids. If Q denotes the heat of neutralization, q the heat of ionization, and a the degree of ionization, $Q=13\cdot52-(1-a)q$. At 2·15°, $a=0\cdot2$; $(1-a)q=-1\cdot242$; Q calculated $=15\cdot06$, observed $=14\cdot98$ Cals. At 35°, $a=0\cdot177$; $(1-a)q=-1\cdot5006$; $Q=14\cdot75$.

E. Cornec[16] gave 1·3507 for the **index of refraction** of the acid soln. of sp. gr. 1·1056. J. H. Gladstone found for the refractive index of soln. of sp. gr. 1·180 at 7·5°, 1·3584, 1·3630, and 1·3746 respectively for the *A*-, *D*-, and *H*-lines. W. J. Pope gave 21·6 for the refraction equivalent of the H_2PO_4-radicle. C. Féry said that in the progressive neutralization of phosphoric acid by sodium hydroxide there are three critical points corresponding with the appearance of the primary, secondary, and tertiary phosphates. E. Cornec found that with potassium hydroxide, there is evidence of the formation of the normal salt and of the dihydrophosphate as shown in Fig. 42, which also includes values for the refraction, $(\mu-1)/D$, and for the sp. gr. D. The results are thought by E. Cornec to be not inconsistent with the formation of complex phosphates, $KH_5(PO_4)_2$; $K_5H_4(PO_4)_3$; and $K_7H_5(PO_4)_4$. When ammonia is used in place of the alkali-lye, the normal and dihydro-salts produce singular points on the curve. J. A. Wasastjerna studied the refraction equivalents of the phosphates. W. W. Coblentz found orthophosphoric acid to be too opaque to obtain other than an imperfect **ultra-red transmission spectrum.**

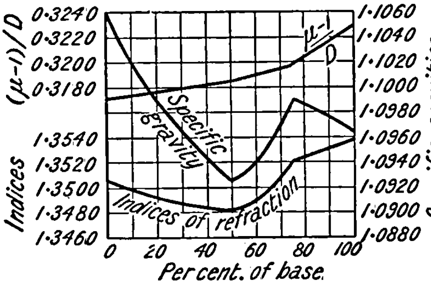


FIG. 42.—Neutralization Curves of Phosphoric Acid.

J. F. Daniell[17] electrolyzed a 6 to 11 per cent. soln. of phosphoric acid in a cell with electrode compartments and obtained the migration value $n=\frac{1}{4}$. M. Faraday tried to electrolyze molten phosphoric acid, but he obtained evidence that only the adsorbed water was decomposed by the current, not the acid itself. Again, according to C. Luckow, aq. soln. of phosphoric acid are not decomposed by the electric current, but if carbon electrodes be employed, A. Bartoli and G. Papasogli say that *phosphomellogen* is formed, and with graphite electrodes, *phosphographitic acid.* According to G. Janecek, when molten phosphoric acid is electrolyzed at a temp. below that at which it begins to lose water, it first forms pyrophosphoric acid, then metaphosphoric acid, then phosphorous acid and phosphine.

According to M. Rabinowitsch,[18] the **electrical conductivity** of orthophosphoric acid, $2H_3PO_4.H_2O$, in the crystalline and surfused states approximates respectively to 10^{-4} and 10^{-2} mhos. The temp. coeff. is positive, and there is an abrupt change on solidification. The decomposition potential is 1·70 volts. The ratio of the electrical conductivities in the crystalline and surfused states is assumed to indicate the degree of loosening of the crystal lattices. The conductivity of the anhydrous acid decreases with time, and is associated with some change in the acid. W. Ostwald found the electrical conductivity of phosphoric acid to be 7·27 when that of hydrochloric acid is 100. The specific and eq. electrical conductivity of soln. of phosphoric acid has been measured at 18° by F. Kohlrausch. The conductivity of soln. of phosphoric acid has also been measured by W. Foster, A. A. Noyes and co-workers, W. Ostwald, C. Déguisne, S. Arrhenius, H. Compton, F. W. Küster and co-workers, D. Berthelot, A. Smith and A. W. C. Menzies, E. B. R. Prideaux, M. Pouchon, H. Wegelins, and G. A. Abbott and W. C. Bray. H. E. W. Phillips used highly purified phosphoric acid and obtained the results indicated in Table V. These are plotted in Fig. 44, along with those for hydrochloric, nitric, and sulphuric acids and for soln. of potassium and sodium hydroxides for comparison. The conductivity of phosphoric acid thus increases with concentration from 1·4 to 38 per cent.; thence to 44 per cent. the increase is slow; it then decreases slowly to about 50 per cent., after which the decrease is as rapid as the former rise. H. Crompton found that the second differential coeff. of the electrical conductivity with the composition of the soln. indicated the presence of $H_3PO_4.7H_2O$ and of $H_3PO_4.2H_2O$—*vide* sulphuric acid. S. Arrhenius found a maximum in the conductivity, λ, with variations of temp. θ. The temp. effect can be represented by $\lambda=\lambda_0e^{-0\cdot0822\theta}(1+0\cdot01455\theta)$,

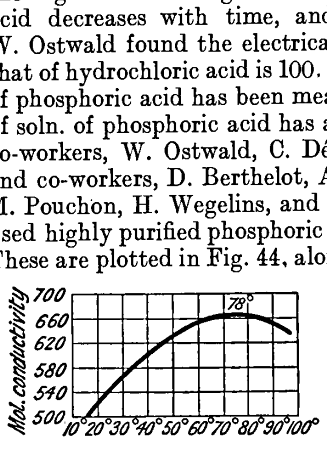


FIG. 43.—The Effect of Temperature on the Electrical Conductivity of Solutions of Phosphoric Acid.

TABLE V.—ELECTRICAL CONDUCTIVITIES OF SOLUTIONS OF PHOSPHORIC ACID.

Percentage concentration.	Equivalents per litre.	Specific resistance.	Specific conductivity.	Molecular conductivity.	Percentage ionization.
1·4	0·43	71·435	0·01400	97·50	40·63
2·87	0·89	39·484	0·02533	85·20	35·50
5·28	1·66	23·553	0·04245	76·60	31·92
16·09	5·37	12·401	0·08064	44·91	18·71
30·71	11·20	7·803	0·12816	34·43	14·35
38·49	14·71	6·853	0·14592	29·77	12·40
43·26	17·03	6·704	0·14916	26·28	10·95
48·90	19·91	6·921	0·14449	21·77	9·07
52·83	22·06	7·272	0·13750	18·70	7·79
65·72	29·92	9·779	0·10226	10·30	4·29
71·29	33·75	12·697	0·07876	7·00	2·92
82·22	42·08	24·670	0·04055	2·89	1·20
92·07	50·42	45·388	0·02203	1·31	0·55
100·03	57·69	71·134	0·01406	1·73	0·30

which is a maximum when $\theta=53°$, but since the conductivity at λ_0 is taken at 25°, the maximum, as in Fig. 43, occurs at 78°. The percentage ionization is also shown in Table V. A. A. Noyes and co-workers found the effect of temp. on the conductivity to be such that for soln. containing M milli-formula weights of H_3PO_4 per litre, the conductivities were as follow :

M	18°	25°	50°	75°	100°	128°	156°
0·0	338	376	510	631	730	839	930
0·2	330·8	367·2	493·0	600·3	688·5	762·1	804·7
2·0	283·1	311·9	400·7	463·6	498·2	507·6	489·0
10·0	203	222	273	300	308	298	274
12·5	191·2	208·1	254·1	278·5	283·9	273·6	250·5
50·0	122·7	132·6	157·8	168·6	167·8	158·0	142·0
80·0	104	112·4	133	141	141	134	118
100·0	96·5	104·0	122·7	129·9	128·4	120·2	107·87

The temp. coeff. is negative at the higher temp. and positive at the lower temp.; this also agrees with the observations of A. N. Campbell on the conductivity of phosphoric acid at 0°, and those of F. Kohlrausch at 18°. A. A. Noyes and co-workers calculated that the percentage **ionization**, a, of soln. of phosphoric acid when the conc. are expressed in milli-formula-weights per litre at 4°.

Conc.	0·0	0·2	2·0	10·0	12·5	50·0	80·0	100·0
a 18°	100	98	84	60	36·5	36·5	31·0	38·5 per cent.
a 156°	100	86·5	52·5	29·4	27·0	15·5	12·5	11·5 ,,

J. Kendall and co-workers also computed values of a from the cryoscopic data. Phosphoric acid is a comparatively weak acid which ionizes in three stages: $H_3PO_4 \rightleftharpoons H^{\cdot}+H_2PO'_4 \rightleftharpoons 2H+HPO_4''$, at moderate dilutions, and even at extreme dilutions it is but partially resolved: $H_3PO_4 \rightleftharpoons 3H^{\cdot}+PO_4'''$. The first hydrogen ion has the strongest acidic function, the third the weakest. G. A. Abbott and W. C. Bray have also measured the ionization constants of orthophosphoric acid and find at 18°:

$H_3PO_4 \rightleftharpoons H^{\cdot}+H_2PO_4'$ . . . . . $K_1=1{\cdot}1\times10^{-2}$
$H_2PO'_4 \rightleftharpoons H^{\cdot}+HPO_4''$ . . . . . $K_2=1{\cdot}95\times10^{-7}$
$HPO''_4 \rightleftharpoons H^{\cdot}+PO_4''$ . . . . . . $K_3=3{\cdot}6\times10^{-13}$

For comparison, the results with carbonic acid and hydrogen sulphide are quoted:

$H_2CO_3 \rightleftharpoons H^{\cdot}+HCO_3'$. $K_1=3{\cdot}0\times10^{-7}$ $H_2S \rightleftharpoons H^{\cdot}+HS'$ . . $K_1=9{\cdot}1\times10^{-8}$
$HCO'_3 \rightleftharpoons H^{\cdot}+CO_2''$. $K_2=6{\cdot}0\times10^{-11}$ $HS' \rightleftharpoons H^{\cdot}+S''$ . . $K_2=1{\cdot}2\times10^{-15}$

M. S. Sherrill and A. A. Noyes gave $K_1=0{\cdot}0083$ when expresssed in terms of the activities at 18°. E. B. R. Prideaux gave for K_2, $1{\cdot}95\times10^{-7}$, and for K_3,

$3{\cdot}0\times10^{-12}$; H. T. S. Britton, $K_1=0{\cdot}0094$; $K_2=1{\cdot}4\times10^{-7}$; and $K_3=2{\cdot}7\times10^{-13}$; E. Blanc, $K_2=8\times10^{-7}$; and $K_3=2{\cdot}3\times10^{-12}$; while E. B. R. Prideaux and A. T. Ward gave $K_2=6\times10^{-8}$, and $K_3=1{\cdot}1\times10^{-12}$. C. Matignon, and G. Gire gave $K_2=1{\cdot}9\times10^{-7}$; and E. Blanc, $K_2=2\times10^{-5}$. I. M. Kolthoff calculated $K_3=5\times10^{-13}$. The ionization constants were also studied by L. V. Rothmund and K. Drucker, A. A. Noyes, and G. W. Eastman, and J. Kendall and co-workers. Hence, orthophosphoric acid behaves like a fairly strong acid with respect to the first eq. of hydrogen; and like a weak acid intermediate between carbonic acid and hydrogen sulphide with respect to the second eq. of hydrogen; and like a very weak acid intermediate between HCO'_3 and HS′ with respect to the third eq. of hydrogen. In the normal phosphates, the third eq. of a base is so feebly combined that it can be displaced even by the dilution of the soluble phosphate with water; normal ammonium phosphate is particularly unstable. E. Blanc obtained the conductivity of a soln. of normal sodium phosphate treated with successive additions of hydrochloric acid and obtained a curve with breaks at $C_H=1{\cdot}1\times10^{-12}$, 4×10^{-11}, and $6{\cdot}5\times10^{-9}$. L. Pessel found that mixture of pyrophospboric and hydrochloric acids show an abnormally low electrical conductivity corresponding with a feebly ionized compound of the two acids; while J. Meyer and A. Pawletta observed that the conductivity of phosphoric acid remains the same with the progressive addition of sulphuric acid, while that of sulphuric acid remains the same with increasing concentration. H. C. Jones and co-workers calculated from the conductivity and f.p. data that in soln. containing M mols of phosphoric acid per litre, the ions are hydrated so that H mols of water are in combination with a mol of the salt at the given concentration:

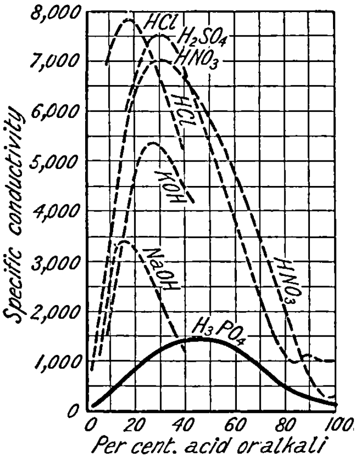


FIG. 44.—Electrical Conductivities of Solutions of Some Acids and Alkalies.

M . .	3·0	4·0	5·0	6·0	6·919
H . .	0·79	2·79	3·95	4·37	4·34

F. H. Jeffery observed that in the electrolysis of 15 per cent. orthophosphoric acid with a gold anode, a little of that metal passes into soln. For the affinity constant, *vide* sulphuric acid.

D. Berthelot showed that when a monobasic acid is treated with progressively increasing amounts of alkali, the electrical conductivity decreases to a minimum which is reached when the acid is neutralized by the base; any further addition of alkali causes the conductivity to increase. This is in agreement with the fact that the conductivity of a salt is in general less than that of its component acid or base. With polybasic acids, a minimum occurs when enough alkali has been added to form a primary salt, the conductivity then increases, and then increases in passing from the primary to the secondary, and from secondary to tertiary salts. The first hydrogen of phosphoric acid was found to behave like a monobasic acid; the second hydrogen, like a slightly ionized weak acid; and the third hydrogen, like the OH-radicle of phenol. These facts agree with the heats of neutralization; the lowering of the f.p.; sp. gr. of soln.; the indices of refraction, and with the behaviour of the acid towards indicators where R. T. Thomson, and E. Salm showed that one eq. may be titrated with methyl-orange as indicator; the second with phenolphthalein, and the third with trinitrobenzene as indicator. Phosphoric acid thus appears to be monobasic with methyl-orange as indicator; dibasic with phenolphthalein, and tribasic with trinitrobenzene. F. W. Küster and co-workers determined the neutralization points of phosphoric acid from conductivity measurements. The curve given by W. M. Clark shows the **hydrogen ion concentration** during the process of the titration of 50 c.c. of 0·1M-H_3PO_4 with 0·1N-KOH. Methyl-orange is sensitive to H˙-ions over the range 3·1 to 4·4p_H, and phenolphthalein, over the range 8·3 to 10·0p_H, and these indicators are therefore applicable for the KH_2PO_4 and K_2HPO_4 stages respectively as shown in the diagram. C. E. Davis and co-workers, W. F. Hoffmann and R. A. Gortner, J. C. Brünnich, and R. Dubrisay formed similar conclusions. W. E. Ringer measured the H˙-ion conc. of dil. soln. of phosphoric acid and of sodium hydrophosphate, and dihydrophosphate. W. F. Hoffmann and R. A. Gortner, K. Täufel and C. Wagner, and G. L. Wendt and A. H. Clarke studied the electrometric titration with calcium hydroxide; and H. T. S. Britton, the electrometric titration of the acid with sodium hydroxide and the alkaline earth hydroxides, as well as of trisodium phosphate soln. with soln. of salts of calcium, beryllium, magnesium, zinc, aluminium, zirconium, thorium, chromium, and manganese. The activity of the phosphate ions was discussed by E. J. Cohn.

The temp. coeff. of the conductivity was measured by F. Kohlrausch, D. Berthelot, S. Arrhenius, and C. Déguisne. For a 10 per cent. soln., when the sp. conductivity at 18° is represented by K_{18}, the temp. coeff. $(dK/dT_{22})/K_{18}$ is 0·0104; for a 50 per cent. soln., 0·0174; and for an 87·1 per cent. soln., 0·0372. A given soln. has a definite temp. for the maximum conductivity, and above that temp., the conductivity decreases. The increasing mobility of the ions with rise of temp. may be compensated by the decreasing ionization. A. A. Noyes found for a 3×0·98 mol. soln., at 12°, 76°, and 93°, respectively, the mol. conductivities 50·2, 71·0, and 69·4 with the temp. coeff. 0·60, 0, and —0·12 respectively. The negative temp. coeff. corresponds with the negative heat of ionization.

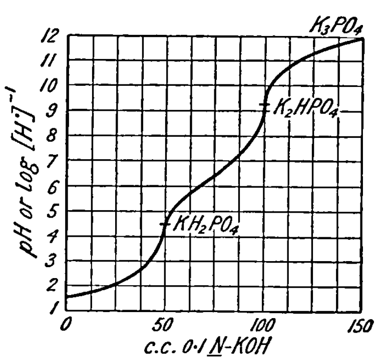
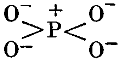


FIG. 45.—The Hydrogen Ion Concentration during the Titration of Phosphoric Acid with Alkali-lye.

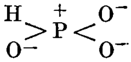
W. Plotnikoff found the mol. conductivity of ethereal soln. diminishes with dilution, and increases with rise of temp. W. Hittorf attempted to determine the **transport number** of the anion in aq. soln. of normal sodium phosphate, but the salt was so much hydrolyzed that most of the current was carried by the alkali. With aq. soln. of sodium hydrophosphate, the transport number of the HPO''_4-anion was 0·516; and with sodium dihydrophosphate for the $H_2PO'_4$-anion, 0·383. J. F. Daniell and W. A. Miller also made some observations with this salt. W. Hittorf found with soln. of potassium dihydrophosphate, the transport number of the $H_2PO'_4$-anion was 0·277. O. Wosnessensky measured the potential difference at the boundary of phosphoric acid and a non-aqueous solvent. P. Pascal studied the magnetic properties. J. Murray tried if he could decompose a soln. of the acid by magnetized iron.

The constitution of phosphoric acid.—The analyses of phosphoric acid by E. M. Péligot,[19] R. Brandes, M. Berthelot, and A. Joly correspond with the hemihydrate. A. Hantzsch found that in sulphuric acid soln. the depression of the f.p. for soln. of different conc. corresponded with mol. wts. ranging from 54 to 78, and therefore, said he, orthophosphoric acid is very strongly ionized in this solvent. On the other hand, according to H. Giran, the f.p. in glacial acetic acid shows that the mol. wt. of orthophosphoric acid in a freshly prepared soln. corresponds with that required for $(H_3PO_4)_2$, but soon approaches that required for H_3PO_4. This phenomenon recalls F. M. Raoult's observation that the mol. wts. of freshly prepared soln. of sulphuric and hydrochloric acids in acetic acid correspond respectively with $(H_2SO_4)_2$ and $(HCl)_2$, and that the molecules depolymerize on standing. Acetic acid, also, has simple molecules CH_3COOH in aq. soln., and doubled molecules $(CH_3COOH)_2$ in benzene soln. D. Balareff found that soln. of ortho- and meta-phosphoric acids slowly form pyrophosphoric acid; and he showed that the vap. densities of methyl and ethyl phosphates agree with the normal values for R_3PO_4. The structural formula for phosphoric acid will depend upon what view is adopted about the valency of phosphorus—ter- or quinquevalent. In the former case, the structural formula will be $HO—O—P{=}(OH)_2$, and $O{=}P{\equiv}(OH)_3$ in the latter. The first formula was suggested by J. Thomsen to explain the peculiar thermal phenomena attending the progressive addition of sodium hydroxide to the acid. The hypothesis is unnecessary since it is more probable that with the three hydrogen atoms the one helps the other in such a way that if one be removed the bonds holding the other two are weakened. P. Pascal also said that the magnetic susceptibilities favour the $PO(OH)_3$ formula for phosphoric acid and $R—PO(OH)_2$ for *phosphinic acid*. The first formula is generally preferred for the following reasons: Phosphoryl chloride must be either $Cl—O—P{=}Cl_2$ or $O{=}P{\equiv}Cl_3$. Phosphorus is undoubtedly quinquevalent in the pentafluoride and also in the pentachloride. From the mode of formation of phosphoryl chloride the formula $O{=}PCl_3$ is usually considered, without direct proof, to be more probable. Phosphoric acid is formed by treating phosphoryl chloride, $O{=}PCl_3$, with water, and therefore $O{=}P{\equiv}(OH)_3$ is the most probable structural formula for phosphoric acid. G. Oddo made an hypothesis in which it is assumed that an atom of hydrogen, in the neighbourhood of two multi-valent elements, can divide its valency between the two by assuming a mean position of stable equilibrium; he symbolizes the valency $-\!\!<$; and calls the phenomenon *mesoidria—mesohydry*. The formula is in agreement with O. Stelling's observations on the *K*-series of the X-ray spectra. T. M. Lowry said that as in the case of the oxy-sulphur acids—*vide* hyposulphurous acid—the most stable acid of phosphorus contains four oxygen atoms. The PO_4'''-ion can be written:



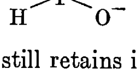
$${}^{O^-}_{O^-}\!\!>\overset{+}{P}<^{O^-}_{O^-}$$

where the atom of phosphorus carries a single positive charge. The corresponding acid with three negatively-charged oxygen atoms is of low stability, being only dibasic:



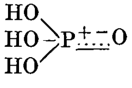
$${}^{H}_{O^-}\!\!>\overset{+}{P}<^{O^-}_{O^-}$$

while hypophosphorous acid with only two negatively-charged oxygen atoms is monobasic:



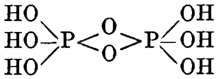
$${}^{H}_{H}\!\!>\overset{+}{P}<^{O^-}_{O^-}$$

and the central phosphorus atoms still retains its positive charge, for this appears to be a necessary condition for stability with nearly all the oxy-acids. H. Burgarth, and H. Remy discussed this subject. E. B. R. Prideaux gave for the electronic structure (*vide infra*, phosphorus pentachloride):



$$\begin{matrix}HO\\HO\\HO\end{matrix}\!\!>P\underset{\cdots}{\overset{+\ -}{}}O$$

The basicity of phosphoric acid appears different when it is neutralized with sodium hydroxide according to the indicator employed—*vide supra*—and the electrical conductivity data explain how the acid was once considered by M. Berthelot and W. Louguinine, A. Joly, D. Berthelot, P. Walden, and J. B. Senderens to be dibasic like sulphuric or oxalic acid, and not tribasic like citric acid. Indeed, there is now little room for doubting the tribasicity of the acid, and E. Cornec's f.p. curves for mixtures of phosphoric acid with different proportions of sodium hydroxide give a minimum for Na_3PO_4, and two folds representing the formation of Na_2HPO_4, and NaH_2PO_4, Fig. 42. If the doubled formula for phosphoric acid —$(H_3PO_4)_2$, that is, $H_6P_2O_8$—be accepted, this acid probably has the constitution:



The doubled formula corresponds (i) with H. Giran's value for the mol. wt. of the acid in acetic acid soln.; (ii) with the formation of A. Joly's hemihydrate, $2H_3PO_4.H_2O$; (iii) with D. Balareff's measurements of the vap. press. of soln. of the ortho-acid on a rising temp. where a marked rise of temp. occurs when the acid dissociates to simple molecules: $(H_3PO_4)_2=2H_3PO_4$; and (iv) with H. Giran's series of salts of the type $M'H_5P_2O_8$; and with E. Filhol and J. B. Senderens salts of the type $M'''H_3P_2O_8$, that is, $M'''PO_4.H_3PO_4$. D. Balareff said that orthophosphoric acid is partly converted into the pyro-acid when kept in a desiccator over phosphoric oxide, or even over sulphuric acid. Orthophosphoric acid has the simple mol. wt. in sulphuric acid soln., and if the free acid had the same constitution, it might be expected that the pyro-acid would also be formed on dissolving in sulphuric acid, but this is not the case. Ethyl and methyl orthophosphates have vapour densities corresponding approximately with the simple formulæ.

According to A. Werner's hypothesis, the molecule of phosphoric acid consists of an atom of phosphorus co-ordinated with four oxygen atoms in accord with the co-ordination number of that element. This group forms the tervalent anion of tribasic phosphoric acid:

$\left[\begin{matrix}\text{O}\\ \text{OPO}\\ \text{O}\end{matrix}\right]^{'''}\text{H}^{\cdot}_{3}$	$\left[\begin{matrix}\text{O}\\ \text{OPH}\\ \text{O}\end{matrix}\right]^{''}\text{H}^{\cdot}_{2}$	$\left[\begin{matrix}\text{O}\\ \text{OPH}\\ \text{H}\end{matrix}\right]^{'}\text{H}^{\cdot}$	$\left[\begin{matrix}\text{H}\\ \text{OPH}\\ \text{H}\end{matrix}\right]$	$\left[\begin{matrix}\text{H}\\ \text{HPH}\\ \text{H}\end{matrix}\right]^{\cdot}\text{I}'$
Phosphoric acid.	Phosphorous acid.	Hypophosphorous acid.	Phosphine oxide.	Phosphonium iodide.

If one of the oxygen atoms be replaced by a hydrogen atom, the bivalent anion of dibasic phosphorous acid is formed; and if another oxygen atom be replaced by hydrogen, the univalent anion of monobasic hypophosphorous acid is formed. The substitution of a third hydrogen atom for an oxygen atom furnishes a neutral group corresponding with POH_3; this compound has not been isolated, but the methyl and ethyl derivatives, $(CH_3)_3PO$, and $(C_2H_5)_3PO$, have been prepared. The substitution of the remaining oxygen atom by hydrogen furnishes the phosphonium cation $PH^{\cdot}_4$. H. E. Armstrong and F. P. Worley made some observations on the constitution of phosphoric acid—*vide* sulphuric acid.

The action of heat on orthophosphoric acid.—In his *Recherches on the Arsenates, Phosphates, and Modifications of Phosphoric Acid*, T. Graham[20] showed that when evaporated at about 149°, a dil. soln. of phosphoric acid gives a syrupy liquid which consists entirely of orthophosphoric acid, and between 150° and 160°, it loses water very slowly. At 238°, it loses water so that the ratio is $P_2O_5 : H_2O = 1 : 2\frac{2}{3}$ instead of 1 : 3 required for the orthophosphatic acid. When evaporated slowly in a platinum flask between 212° and 213°, the ratio was reduced to $1 : 2\frac{1}{3}$ because a very large proportion is converted into pyrophosphoric acid, $H_4P_2O_7$. At the greatest heat of a sand-bath—considerably higher than the m.p. of lead—the proportion of water was reduced to a little less than 1 : 2, and the product consisted largely of meta-phosphoric acid. G. Tammann found that if orthophosphoric acid be heated until it begins to fume, pyrophosphoric acid is formed; and by further heating, there is obtained a liquid which, on cooling, forms a white fibrous mass of metaphosphoric acid. The conversion to pyrophosphoric acid, says G. Watson, is not complete between 230° and 235°, but is so between 255° and 260°; the formation of the meta-acid begins between 290° and 300°. The vap. press. measurements of D. Balareff show that orthophosphoric acid probably has the formula $(H_3PO_4)_2$, and when heated in a closed vessel, there is an equilibrium reaction, $(H_3PO_4)_2 \rightleftharpoons H_4P_2O_7 + H_2O$, and that with a rising temp. $H_4P_2O_7 \rightleftharpoons 2HPO_3 + H_2O$ occurs. In addition, there is the depolymerization: $(H_3PO_4)_2 \rightleftharpoons 2H_3PO_4$, and this is followed by $H_3PO_4 \rightleftharpoons H_2O + HPO_3$. D. Balareff's results for the vap. press. of the dehydrating orthophosphoric acid at different temp., and the formation of pyro- and meta-phosphoric acids are shown in Fig. 46. The volatility of the metaphosphoric acid prevented the completion of its curve, but sufficient remains to show that the reaction, $(H_3PO_4)_2 \rightleftharpoons H_4P_2O_7 + H_2O$, is reversible, and the proportion of pyrophosphoric acid formed at any given temp. is diminished by increasing the vap. press. of the water in the system. Similar remarks apply to the formation of metaphosphoric acid from the pyro-acid: $H_4P_2O_7 \rightleftharpoons H_2O + 2HPO_3$. The dissociation of the doubled molecule of the ortho-acid: $(H_3PO_4)_2 \rightleftharpoons 2H_3PO_4$, with rising temp. leads to the supposition that metaphosphoric acid might be produced directly from the ortho-acid: $H_3PO_4 \rightleftharpoons HPO_3 + H_2O$, but this reaction has not yet been demonstrated. According to M. Berthelot and G. André, during the dehydration of orthophosphoric acid, there is probably a state of equilibrium between the three acids—ortho-, pyro-, and meta-phosphoric acids—dependent upon the temp., so that if the temp. of dehydration is different, the product obtained by dissolving the calcined mass in water will be different. The action must be complex. For instance, when a mixture of meta- and orthophosphoric acids is heated (on a water-bath), the pyro-acid is formed: $HPO_3 + H_3PO_4 = H_4P_2O_7$.

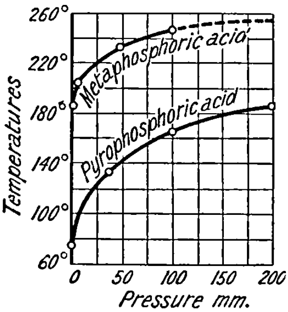


FIG. 46.—Vapour Pressures of Pyro- and Meta-phosphoric Acids.

J. J. Berzelius found that some acid is volatilized when phosphoric acid is heated in an open crucible, but not in a covered crucible, and H. Rose showed that in an open vessel all the phosphoric acid can be volatilized. J. B. Bunce said that some acid is volatilized with the steam, but G. C. Wittstein, and C. R. Fresenius showed that this is not the case when phosphoric acid is evaporated in an open dish, although some of the evaporating liquor may be carried away mechanically if the ebullition is rapid. E. Lautemann, S. Leavitt and J. A. Leclerc, and G. Lechartier have studied the loss of phosphoric oxide during the calcination of ash—about 2·14 per cent. was lost at low redness, 2·08 at bright redness. According to R. Bunsen, phosphoric acid is 23 times more volatile than sodium carbonate.

The chemical properties of orthophosphoric acid.—W. Müller-Erzbach[21] has discussed the affinity of the metals for phosphoric acid. J. Thomsen found the avidity of a mol. of phosphoric acid for one of sodium hydroxide to be a quarter of the value of that for hydrochloric acid. The affinity of phosphoric acid for the bases is greater than that of carbonic acid, boric acid, phosphorous acid, and hypophosphorous acid. The catalytic action of phosphoric acid on the reaction between bromic and hydriodic acids has been studied by W. Ostwald; on the reaction between iodic and sulphurous acids, by R. Höpke; and A. Purgotti and L. Zanichelli on hydrazine sulphate, $N_2H_4.H_2SO_4$. According to W. Ostwald, the velocity constant for the inversion of cane sugar by phosphoric acid is 6·21 when the value for hydrochloric acid is 100; and J. Spohr showed that the presence of neutral salts at 25° retards, or at 40° completely suppresses, the activity of phosphoric acid.

C. R. Fresenius observed no signs of reduction when phosphoric acid is heated in a stream of **hydrogen,** or if in the presence of hydrogen *in statu nascendi.* W. Ipatieff found that phosphoric acid is reduced to phosphorus at 350°–360°. According to W. Ipatieff and W. Nikolaieff, free phosphoric acid and its alkali salts are not affected by hydrogen under high press. and at an elevated temp., but ferric phosphate gives a series of crystalline complex phosphates: $Fe'''_nFe''_mPO_4.xH_2O$, depending on the conditions, and resembling the vivianites. Lead phosphate with hydrogen at 250 to 300 atm. and 360° to 400°, forms a colloidal, orange hemioxide, Pb_2O, and hypophosphorous acid, but with watergas at 400 atm., some phosphine, and lead are formed. The behaviour of soln. of phosphoric acid in **water** towards indicators has been discussed above —*vide* also Table VI. H. E. W. Phillips said that the 100 per cent. acid does not react with litmus. M. Berthelot and G. André found the partition coeff. of phosphoric acid between water and ether is such that the concentration in ether =2700 : 1, with a 8·33 per cent. aq. soln.; this ratio is 2900 : 1 with a 30 per cent. soln., with a very conc. soln. of phosphoric acid ether is attacked, forming a compound with the evolution of heat, and ether may be added in any proportion causing a precipitation. If a small quantity of water is added, it mixes completely, but if the addition of water is continued, there at last comes a point when a small quantity of ether separates, highly charged with phosphoric acid. The addition of more water causes the separation of a larger vol. of ether containing a lower proportion of acid, and still more water separates a still larger vol. of ether containing still less acid, and this change continues as the addition of water is continued, until the partition coeff. already stated is reached. D. Balareff observed that a soln. of orthophosphoric acid slowly forms pyrophosphoric acid on keeping. According to W. F. Hillebrand and G. E. F. Lundell, no volatilization losses of phosphorus occur during evaporation of sulphuric acid soln. of phosphates, provided the evaporation is carried on at 150° and stopped when fumes appear. Volatilization losses of phosphorus from sulphuric acid soln. of phosphates may occur during evaporation to complete expulsion of sulphuric acid, during evaporation at high temperatures, such as 200°–260°, and by unduly prolonged evaporation above 150°. M. Berthelot and G. André did not observe any signs of reduction when phosphoric acid is heated with **acids** at 100°. According to F. Flichter and W. Bladergroen, soln. of phosphoric acid, after treatment with fluorine, immediately precipitate iodine from iodides. A slight additional precipitate occurs in one or two cases on keeping. The oxidizing power is attributed principally to permonophosphoric acid, H_3PO_5. The soln., and also permonophosphoric acid prepared by the action of hydrogen peroxide on phosphorus pentoxide, oxidized manganous sulphate to violet manganic phosphate, and not to permanganate as suggested by J. Schmidlin and P. Massini. The action of fluorine on di- or tri-alkali phosphates and on pyrophosphates, produced salts of both permonophosphoric acid and perphosphoric acid, $H_4P_2O_8$ (precipitated in two stages); the former is unstable, so that it was possible to obtain perphosphoric acid mixed with potassium fluoride from the soln. If **hypochlorites** are evaporated with conc. phosphoric acid, A. J. Balard said that hypochlorous acid and some chlorine are formed; as well as a little chloride. P. Chrétien prepared a complex with **iodic acid,** namely, *phosphatoiodic acid,* $P_2O_5.18I_2O_5.4H_2O$, in needle-like crystals by boiling syrupy phosphoric acid with an excess of iodic acid. The product is rapidly decomposed by moist air. Fine crystals of ammonium phosphatoiodate, $4(NH_4)_2O.P_2O_5.18I_2O_4.12H_2O$; lithium phosphatoiodate, $3Li_2O.P_2O_5.11H_2O$; sodium phosphatoiodate, $6Na_2O.P_2O_5.18I_2O_5.5H_2O$; and potassium phosphatoiodate, $4K_2O.18I_2O_5.5H_2O$, were obtained by adding iodic acid, in small portions at a time, to boiling syrupy phosphoric acid in which the alkali dihydrophosphate had been dissolved, and slowly cooling to liquid.

P. N. Raikow found that phosphoric acid dissolves **sulphuric acid** at ordinary temp., and when the soln. is heated to 350° some sulphur dioxide is evolved. The phosphates are all decomposed by treatment with sulphuric acid. R. H. Adie, and C. Friedheim prepared complex compounds of sulphuric and phosphoric acids —*vide infra,* phosphoryl hydrosulphate. H. Prause prepared complexes with **telluric acid**—*e.g.* $(NH_4)_4P_2TeO_{10}$. H. Reinsch found that syrupy phosphoric acid absorbs **nitric oxide,** and forms a crystalline mass when cooled to —20°; the product may be a compound. According to E. Divers, phosphoric acid does not act very vigorously on a soln. of **ammonium nitrate** in ammonia. F. D. Chattaway and H. P. Stevens found that phosphoric acid decomposes **nitrogen iodide,** producing ammonia. According to A. Geuther, when phosphoric acid is treated with **phosphorus pentachloride** at ordinary temp., phosphoryl chloride and hydrogen chloride are formed; **phosphorus trichloride** furnishes metaphosphoric and phosphorous acids; and **phosphoryl chloride** is without action in the cold, but when hot, metaphosphoric acid is formed if the phosphoryl chloride be in excess, and phosphorous acid if only a little be present. G. Meyer, and A. Vogel prepared a complex with **boric oxide** or **boric acid**—*vide* boron phosphate, **5**. 32, 27.

When heated with **carbon,** the phosphates of the heavy metals are generally changed into phosphides; the phosphates of the alkali and alkaline earth metals are not decomposed except at temp. exceeding 1200°—*vide supra,* the preparation of phosphorus. M. Dubinin studied the adsorption of phosphoric acid by carbon; P. Carré, the action of phosphoric acid on **alcohol**; J. Heimann, on **cetyl alcohol**; A. Benrath, on **sodium ethoxide**; P. N. Raikow and P. Tischkoff, on **esters**; M. Berthelot and G. André, and M. Rabinowitsch and S. Jakubsohn, on **ether**; P. Carré, on **glycol**; and H. Imbert and G. Belugou, P. Carré, G. Prunier, L. A. Adrian and J. A. Trillat, A. Contardi, F. B. Power and F. Tutin, on **glycerol.** If glacial phosphoric acid and glycerol be heated to 100°, the product neutralized with barium carbonate, and the filtered soln. decomposed with the calculated amount of sulphuric acid, *glycerophosphoric acid,* $CH_2OH.CHOH.CH_2O.PO(OH)_2$, is formed. This acid forms normal and acid salts with the metals, and combines with organic bases like quinine. O. Meyerhof and J. Suranyi measured the ionization constants of glycerophosphoric, and hexosediphosphoric acid; and P. Fleury and Z. Sutu, the hydrolysis of the α- and β-glycerophosphoric acids. W. Ostwald, J. Spohr, and J. R. Duggan investigated the action of phosphoric acid on **sugars**; L. Portes and G. Prunier, and P. Carré, on **mannitol**; P. Carré, on **erythritol**; P. N. Raikow and R. Tischkoff, on **sulphanilic acid,** and **sulphosalicylic acids**; C. Friedel and J. M. Crafts, on **aromatic sulpho-acids**; D. Vorländer and A. J. Perold, on **wool**; W. W. Worms, A. A. Panormoff, and G. S. Johnson, on **albumin**; and W. Reidemeister, on **agar-agar.** If phosphoric acid or a phosphate be treated in the presence of carbonaceous matters, some phosphoric oxide may be lost. According to P. L. Dulong, and A. J. Balard, if phosphoric acid be heated in **porcelain** crucibles, the glazing is strongly attacked, and the acid so contaminated with alkali, silica, and alumina; if **platinum** crucibles are used, and organic matter or other reducing agents be present, the acid may be reduced and the phosphorus which is liberated will form an easily fusible phosphide with the metal. This may occur during the calcination of phosphatic precipitates —*e.g.* magnesium pyrophosphate—as shown by W. C. Heraeus, and W. P. Headdon. F. Mylius found that phosphoric acid attacks **quartz** vessels above 300°. P. Hautefeuille and J. Margottet found that **silica** dissolves fairly readily in phosphoric acid—about 5 per cent. at 260° —*vide* **6**. 40, 57; O. Nielsen made a partial examination of the ternary system, CaO–SiO_2–P_2O_5; and G. Saring prepared a series of complex salts of the type $Ca_3(PO_4)_2(CaO)_2(K_2O)_2SiO_2$, with the SiO_2 replaced by TiO_2, ZrO_2, CeO_2, ThO_2, SnO_2, PbO_2, $\frac{1}{2}B_2O_3$, $\frac{1}{2}Al_2O_3$, $\frac{1}{2}V_2O_3$, and MoO_3. P. Hautefeuille and J. Margottet prepared complexes with **titania, zirconia,** and **stannic oxide.** E. Wedekind and H. Wilke studied the adsorption of phosphoric acid by zirconia gels; and H. von Euler and E. Erikson, by **alumina** gel. K. Hüttner has studied the action of phosphoric acid on different **silicates.**

According to P. Thénard, and L. N. Vauquelin, when heated with **potassium** or **sodium,** the phosphates furnish alkali phosphides (*q.v.*). W. Smith reported that conc. or dil. phosphoric acid attacks **aluminium** with the evolution of hydrogen; H. Beyers and M. Darrin have studied the passivity of **iron** in phosphoric acid;

and F. Clarkson and H. C. Hetherington the corrosion of iron by the acid. T. Byrom found that **ferrosilicon, spiegeleisen, ferrochrome, ferrotitanium, ferromanganese, ferrovanadium, titanium nitride,** and **chromite** are dissolved by phosphoric acid of sp. gr. 1·75; and M. Wunder and B. Janneret found finely-divided **silicon** is dissolved in a few hours by phosphoric acid, sp. gr. 1·75, at 230°; **zirconium** is dissolved in a few minutes; **tungsten** takes a little longer; and **carborundum** is entirely decomposed in about three hours, while the carbon in these alloys remains undissolved. M. Berthelot found that phosphoric acid reacts with **potassium chromate:** $2H_3PO_4+2K_2CrO_4=2KH_2PO_4+K_2Cr_2O_7+H_2O+3\cdot42$ Cals. at 8°; P. Sabatier also found that chromates are almost completely decomposed by phosphoric acid; and C. Friedheim prepared complexes of **chromic acid** and phosphoric acid. Complexes are also obtained with **tungstic, molybdic, and vanadic acids.** P. Hautefeuille and J. Margottet found that at 100°, phosphoric acid dissolves about 15 per cent. of **ferric oxide,** or 8 per cent. of **alumina,** and if the soln. be maintained at this temp. for some time, crystals of the phosphates separate out. The insoluble phosphates are decomposed, wholly or in part, by fusion with **sodium carbonate.** H. E. W. Phillips said that the 100 per cent. acid does not react with sodium carbonate. W. C. Taber has investigated the solubility of **calcium sulphate** in phosphoric acid; J. Stoklasa, the action of phosphoric acid on **calcium phosphate;** and M. Berthelot, and A. Benrath, on **alkaline earth chlorides.** F. de Lalande and M. Prud'homme noticed the evolution of chlorine when phosphoric acid is heated with **sodium chloride.** M. Weilandt studied the action on the **alkaline earth carbonates,** A. Quartaroli, C. Blarey, A. Joly, and M. Berthelot, the action on the **alkaline earth oxides and hydroxides,** and **magnesia.** S. Bodforss studied the electrometric titration of phosphates with a soln. of a **uranyl** salt.

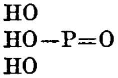
J. T. Meckstroth [22] showed that the largest use for phosphoric acid is in sugar defecation. It is also used in the manufacture of jellies, preserves, and soft drinks; in pharmaceutical preparations; and in the rust-proofing of iron. The chief phosphates in industry are the calcium hydrophosphates used in making baking-powder, and self-rising flour; sodium phosphates used in making boiler compounds, in laundry work, etc. The superphosphates are used in fertilizers. Calcium orthophosphate is the form of bone ash extensively used in the manufacture of bone china.

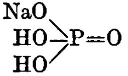
The physiological action of the phosphoric acids.—The alkali phosphates have the remarkable property of nearly preserving their neutrality in the presence of relatively large amounts of acid. For if a little acid be added to a soln. of sodium hydrophosphate, with its $H^{\cdot}$-ion conc. of $0\cdot0_{12}36$(HCl unity), enough acid must be added to convert all the salt to the dihydrophosphate, with its $H^{\cdot}$-ion conc. of $0\cdot0_{6}2$, before the faint acidity of the dihydrophosphate is apparent; and conversely, enough alkali-lye must be added to a soln. of dihydrophosphate before the faint alkaline reaction of the hydrophosphate is apparent. All mixtures of the two salts are more nearly neutral than either alone. L. J. Henderson,[23] and others have discussed the bearing of these facts on the effect of acid on the protoplasm containing the hydrophosphates. The acid forms dihydrophosphate, and through the ready diffusibility of the dihydrophosphate, emphasized by R. L. Maly, the cells eliminate this phosphate which, entering the blood stream, passes out of the body through the kidneys. L. J. Henderson and co-workers added:

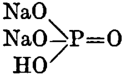
> It can hardly be doubted that the cell will endeavour to restore the normal ratio between potassium di- and mono-phosphates in view of the desirability of restoring the full normal power to neutralize acids. Moreover, though a considerable increase in the amount of phosphate at the expense of the other salt must involve a very slight changes in hydrogen ionization at most, even this slight change can hardly be without influence upon the delicate catalytic reactions of protoplasm. Moreover, too, slight changes of this sort probably influence the colloidal organization of protoplasm to a certain extent. Finally, it is clear that if acid is to be removed from protoplasm without preparatory chemical change it must leave in the form of potassium dihydrophosphate chiefly, for there can be no doubt that in this form chiefly it exists in protoplasm.

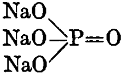
A. B. Poggiale [24] reported that dil. soln. of ortho-, pyro-, or meta-phosphoric acid are not poisonous, while conc. soln. behave like other strong acids. N. Sieber found that 0·5 per cent. hinders putrefaction, but fungi grow in the presence of a soln. of one per cent. of the acid. A. G. Salamon and W. de Vere Mathew found that large quantities of phosphoric acid hinder the growth of yeast. M. Paquelin and L. Jolly showed that pyrophosphates augment the flow of urine and act as diuretics. O. Schulz found that subcutaneous injections of phosphoric acid acted as a poison on rabbits. The subject was also studied by A. Desgrez and B. Guende, E. B. Hart and co-workers, M. Hayduck, M. Kochmann, P. Miquel, E. Moufang, and M. Rosenblatt and M. Rozenbrand.

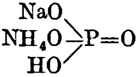
The orthophosphates.—Orthophosphoric acid forms three salts, normal or tertiary, secondary, and primary phosphates, according as all, two, or one of its hydrogen atoms is replaced by an equivalent radicle.[25] The hydrogen atoms may be replaced by different radicles. Thus, the secondary acid salt—ammonium sodium hydrogen phosphate, also called microcosmic salt—is illustrated by the subjoined graphic formula along with the formulæ for the acid and the primary, secondary, and tertiary sodium salts:


Orthophosphoric acid.

Primary.

Sodium dihydrogen phosphate.

Secondary.

Disodium hydrogen phosphate.

Tertiary.

Normal sodium phosphate.

Secondary.

Microcosmic salt.

The tertiary alkali salts are strongly alkaline, the secondary salts are feebly alkaline, and the primary salts feebly acid. The behaviour of the sodium salts towards indicators, shown in Table VI, is interesting.

TABLE VI.—BEHAVIOUR OF SODIUM PHOSPHATES TOWARDS INDICATORS.

Sodium orthophosphate.	Methyl orange.	Phenolphthalein.	Litmus.	Porrier's blue.
Na_3PO_4 . . .	alkaline	alkaline	alkaline	neutral
Na_2HPO_4 . . .	alkaline	neutral	alkaline	neutral
NaH_2PO_4 . . .	neutral	acid	acid	acid

Orthophosphoric acid also forms three series of esters,[26] *e.g.*, **triethyl phosphate,** $(C_2H_5)_3PO_4$, or *phosphoric ether*, is a neutral liquid, insoluble in water; it boils at 215°, and has a sp. gr. 1·072, at 12°; the **diethyl phosphate,** $(C_2H_5)_2HPO_4$, or *diethylphosphoric acid*, acts as a monobasic acid; and **monoethyl phosphate,** $(C_2H_5)H_2PO_4$, or *ethylphosphoric acid* as a dibasic acid.

The orthophosphates are obtained by the direct action of the acid on the basic oxide, hydroxide, or carbonate; and the less soluble phosphates are obtained by double decomposition. While the soluble phosphates form tertiary, secondary, and primary phosphates, the tertiary phosphates of most of the heavy metals have been alone prepared. Consequently, tertiary phosphates are usually prepared by double decomposition—*e.g.* lead orthophosphate, $Pb_3(PO_4)_2$, is precipitated by mixing soln. of lead acetate and disodium hydrogen phosphate. Thallous phosphate and the phosphates of the alkali family of metals, with the exception of lithium, are soluble in water; the remaining phosphates are sparingly soluble, but are usually soluble in dil. nitric acid, and also in aq. soln. of the ammonium salts. The soluble tertiary and secondary phosphates usually have an alkaline reaction, and they can be distinguished by treating a soln. of the salt with calcium chloride, washing the precipitate with water, and warming it with aq. ammonia. A secondary phosphate is thus transformed into the tertiary salt. The phosphoric acid freed during the transformation of the $CaH(PO_4)_2$ will be found in the ammoniacal liquid; whereas, if the tertiary salt has been precipitated, no appreciable amount of phosphoric acid would be found in the ammoniacal liquid. The tertiary orthophosphates of the fixed bases are not decomposed by heat; but when a monohydrogen or secondary phosphate is heated, it forms a pyrophosphate and water; and when a dihydrogen or primary phosphate is heated, it forms a metaphosphate and water. The orthophosphates are described in connection with the individual elements.

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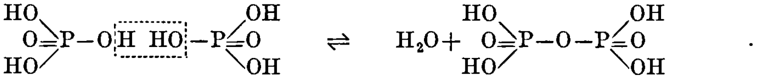
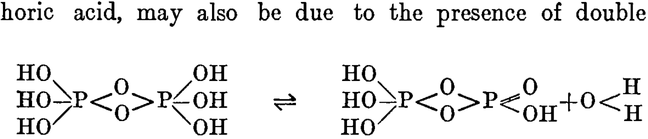
§ 25. Pyrophosphoric Acid

In 1828, T. Clark,[1] first prepared sodium pyrophosphate. He observed with surprise that with sodium phosphate specially purified by heat he obtained a white not a yellow precipitate with silver nitrate, and added, " it was natural to conjecture that sodium phosphate, in its ordinary state, contains some impurity to occasion the yellowness of the precipitate." He subsequently found that when he used sodium phosphate which had been dried at a red-heat, the white precipitate was occasioned by some alteration in the sodium phosphate which was produced by heat. The soln. of the salt which had been heated red hot gave a crop of crystals different in form from those obtained with ordinary sodium phosphate. These crystals were examined by W. Haidinger. He was then able to show that by simply drying the common sodium phosphate, and heating it to redness, an entirely new salt is produced, and added: " This new salt I shall call *pyrophosphate of soda*, a provisional name which it will probably be well to retain, till all doubts are removed respecting the constitution of this salt." Free acid and its salts were made by J. L. Gay Lussac in 1829; by F. Stromeyer in 1830; and by A. Schwarzenberg in 1847. As previously indicated in studying the action of heat on orthophosphoric acid, T. Graham, G. Tammann, G. Watson, and M. Berthelot and G. André obtained the pyro-acid by heating the ortho-acid between 250° and 260°. Two mols. of orthophosphoric acid lose one mol. of water, and the reaction has been graphically symbolized:



The formation of pyrophosphoric acid as the first product of the dehydration of orthophosphoric acid, may also be due to the presence of double molecules, $(H_3PO_4)_2$:



Orthophosphoric acid can thus be regarded as a hydrate, $H_4P_2O_7.H_2O$, of pyrophosphoric acid, and pyrophosphoric acid in turn as a hydrate of the meta-acid, in harmony with the view that pyrophosphoric acid is intermediate between ortho- and meta-phosphoric acids.

M. Berthelot and G. André did not obtain pyrophosphoric acid by heating the ortho-acid with acids at 100°; nor did E. B. R. Prideaux[2] obtain it by the action of an excess of water at room temp. on phosphorus pentoxide. A. Geuther, and A. Joly prepared pyrophosphoric acid by heating on a water-bath an aq. mixture of the two acids: $H_3PO_4+HPO_3=H_4P_2O_7$. F. Schwarz also made pyrophosphoric acid by heating triphosphoric acid with a small quantity of water: $2H_5P_3O_{10}+H_2O=3H_4P_2O_7$. According to A. Geuther, when an excess of phosphoric acid is treated with phosphoryl chloride, $POCl_3$, the pyro-acid is formed: $POCl_3+5H_3PO_4=3H_4P_2O_7+3HCl$; if the phosphoryl chloride be in excess, meta-acid, HPO_3, is formed: $POCl_3+2H_3PO_4=3HPO_3+3HCl$. Pyrophosphoric acid is also formed by the action of phosphorous chloride, PCl_3, on orthophosphorous acid, when some phosphorus is formed at the same time. E. Giana said that phosphates are converted into pyrophosphates when heated to about 800° in a current of air and sulphur dioxide: $Ca_3(PO_4)_2+SO_2+O=CaSO_4+Ca_2P_2O_7$. Sodium pyrophosphate is formed when sodium hydrophosphate is heated: $2Na_2HPO_4=H_2O+Na_4P_2O_7$. When a soln. of normal sodium pyrophosphate is treated with lead nitrate or acetate, lead pyrophosphate, $Pb_2P_2O_7$, is precipitated. C. D. Braun obtained an aq. soln. of the acid from this salt. The lead salt was suspended in ice-cold water; decomposed by a stream of hydrogen sulphide; and the dissolved gas expelled by a current of air, and by agitation for some time with an excess of lead pyrophosphate. The clear soln. of pyrophosphoric acid cannot be well concentrated by evaporation because it is transformed into the ortho-acid during the operation. The liquid can be concentrated by fractional freezing. H. Giran[3] obtained solid pyrophosphoric acid by the action of dry hydrogen chloride on silver pyrophosphate, $Ag_4P_2O_7$, prepared in a similar manner to the corresponding lead salt.

The physical properties of pyrophosphoric acid.—As usually prepared, it is a syrupy liquid. T. Graham prepared pyrophosphoric acid as a soft glass by the evaporation of the aq. soln.; E. M. Péligot, and E. Zettnoff thought that they had obtained the acid in opaque crystals resembling glucose during the slow hydration of metaphosphoric acid. H. Giran found that syrupy pyrophosphoric acid yields white crystalline needles if it be kept about three months at —10°, but H. Giran believes that there is something wrong because the syrupy liquid is undercooled at ordinary temp. and crystallization occurs only when the liquid is seeded with other crystals of the acid, or by the prolonged action of cold. Even then the liquid is so viscid that crystallization occurs very slowly. According to H. Giran, these crystals have a **melting point** not lower than 61°, and a **heat of fusion,** —2·12 Cals. H. Giran found two minima on the f.p. curve of mixtures of water and pyrophosphoric acid—one at 23° with the eutectic $H_4P_2O_7+1{\cdot}25H_2O$, and the other at —75° with $H_4P_2O_7+6{\cdot}87H_2O$. The latter is probably the cryohydric temp. The maximum at 26° corresponds with **hydrated pyrophosphoric acid,** $H_4P_2O_7.1\frac{1}{2}H_2O$, which has been isolated in acicular crystals and which is less stable than that of the ortho-acid into which it readily passes. The dotted curve, Fig. 40, represents the f.p. curve of the binary system, pyrophosphoric acid and water. E. Cornec measured the **lowering of the freezing point** of pyrophosphoric acid by the progressive addition of potassium hydroxide, and the resulting curve showed singular points corresponding with the secondary, tertiary, and quaternary salts. The **index of refraction** of pyrophosphoric acid is 1·3435, and the value is lowered to a minimum, 1·3404, when 50 per cent. of potassium hydroxide has been added. Analogous results were obtained with aq. ammonia in place of potash-lye.

H. Giran's values, for the **heat of formation,** are $(2P,7O,4H)=H_4P_2O_{7\text{liq.}}+529{\cdot}94$ and 533·40 Cals.; $H_4P_2O_{7\text{solid}}$, 532·23 and 535·69; and $H_4P_2O_{7\text{soln.}}$, 540·16 and 543·62 Cals.; $H_4P_2O_{7\text{solid}}+1{\cdot}5H_2O_{\text{liq.}}=H_4P_2O_{7\text{solid}}+3{\cdot}44$ Cals.; and $H_4P_2O_{7\text{solid}}+1{\cdot}5H_2O_{\text{solid}}=H_4P_2O_{7\text{solid}}+1{\cdot}34$ Cals. H. Giran also gives for the **heat of solution,** $H_4P_2O_{7\text{solid}}+$aq. 7·78 and 7·93 Cals. $H_4P_2O_7.1\frac{1}{2}H_2O_{\text{solid}}+\text{aq.}=4{\cdot}49$ Cals., and $H_4P_2O_7.1\frac{1}{2}H_2O_{\text{liq.}}+\text{aq.}=7{\cdot}063$ Cals. H. Giran gives for the **heat of transformation** into orthophosphoric acid with liquid water: $H_4P_2O_{7\text{liq.}}+\text{aq.}=2H_3PO_{4\text{aq.}}+14{\cdot}47$ Cals.; $H_2P_2O_{7\text{liq.}}+H_2O$; $2H_3PO_{4\text{liq.}}+9{\cdot}09$ Cals.; $H_4P_2O_{7\text{solid}}+\text{aq.}=2H_2PO_{4\text{aq.}}+12{\cdot}35$ Cals.; $H_4P_2O_{7\text{solid}}+H_2O=2H_3PO_{4\text{solid}}+6{\cdot}97$ Cals.; $H_4P_2O_{7\text{aq.}}+H_2O=2H_3PO_{4\text{aq.}}+4{\cdot}25$ Cals. J. Thomsen gives for the **heat of neutralization,** $H_4P_2O_{7\text{aq.}}+nNaOH_{\text{aq.}}$, for $n=1$, 14·4 Cals.; for $n=2$, 28·6 Cals.; for $n=4$, 52·7 Cals.; and for $n=6$, 54·5 Cals. H. Giran also found for the first mol of sodium hydroxide, 15·29 Cals.; for the second, 15·65 Cals.; for the third, 13·11 Cals.; and for the fourth, 7·84 Cals.

For soln. containing C mols of the acid $H_4P_2O_7$ per litre, the mol. **electrical conductivity,** μ, found by G. A. Abbott and W. C. Bray, at 18°, is:

C . . .	0·05	0·025	0·0125	0·005	0·0025	0·00125
μ . . .	353·8	384·9	438·6	503·3	556·7	602·0

and for the primary, secondary, tertiary, and quaternary salts, they obtained :

	C	0·1	0·05	0·02	0·01	0·003	0·001	0·0003
μ	$NaH_3P_2O_7$	152·6	181·7	228·7	269·2	269·6	388·6	420·0
	$Na_2H_2P_3O_7$	107·0	120·0	133·2	143·0	156·1	166·0	176·1
	$Na_3HP_2O_7$	148·9	172·1	199·0	220·1	248·7	271·4	288·3
	$Na_4P_2O_7$	156·5	185·2	223·9	256·6	314·3	372·1	420·0

The results for the pyro-acid are so much like those for hypophosphoric acid, that E. Cornec argued a like complexity for the molecules of the two acids. G. A. Abbott and W. C. Bray calculated that with soln. containing c millimols of pyrophosphoric acid per litre, the **degree of ionization,** and the **ionization constants,** are :

c	50	25	12·5	5	2·5	1·25
Primary ionization	86	87	90	92	94	96 per cent.
$H_3P_2O'_7$-ions	34·3	15·6	6·73	2·02	0·75	0·27
$H_2P_2O_7$-ions	8·7	6·15	4·52	2·58	1·60	0·93
$H_4P_2O_7$-mols.	7·0	3·25	1·25	0·40	0·15	0·05
K_1	0·0132	0·0110	0·0106	0·0095	0·0084	0·0073
K_2	0·253	0·134	0·085	0·036	0·020	0·011

showing that the constants decrease with decreasing ionic conc. The ionization constant for $H_4P_2O_7=H_3P_2O'_7+H^\cdot$ is $K_1=0\cdot14$; for $H_3P_2O'_7=H_2P_2O''_7+H^\cdot$ is $K_2=0\cdot011$; for $H_2P_2O'_7=HP_2O'''_7+H^\cdot$ is $K_3=0\cdot0_629$; and for $HP_2O'''_7=P_2O''''_7+H^\cdot$ is $K_4=0_836$. I. M. Kolthoff obtained $K_3=3\cdot6\times10^{-9}$ to $4\cdot6\times10^{-9}$; and $K_4=7\cdot6\times10^{-7}$. W. Hittorf found the **transport number** of normal sodium pyrophosphate in aq. soln. to be 0·645.

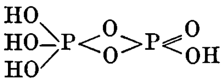
The hydration of pyrophosphoric acid.—T. Graham kept an aq. soln. of dil. pyrophosphoric acid for six months without change ; but, when heated, it was converted into the ortho-acid. The hydration of dil. soln. of pyrophosphoric acid is therefore slow at ordinary temp., but it is rapid when boiled. M. Berthelot and G. André [4] found that a soln. of pyrophosphoric acid contained after standing :

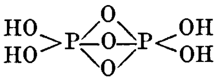
	5	10	19	52	89	110	121 days
$H_4P_2O_7$	87	83	76·5	69·5	58	49·5	43·1
H_3PO_4	4	8	14·5	21·5	33	41·5	47·9

There was no sign of the formation of any metaphosphoric acid ; the more conc. the soln. the faster the change, or the more dil. the soln. the greater the stability. P. Sabatier found that the presence of a strong acid—sulphuric or hydrochloric acid—accelerates the hydration, while a weak acid—*e.g.* acetic acid—retards the conversion. C. Montemartini and U. Egidi found the reaction is of the first order : $H_4P_2O_7+aq.=2H_3PO_{4aq.}$. The speed of hydration is faster than with metaphosphoric acid. The speed of hydration has also been measured by G. A. Abbott, who found that the rate is nearly ten times faster at 100° than it is at 75°. L. Pessel found that the rate of hydration is accelerated by $H^\cdot$-ions ; and that mixtures with hydrochloric have a low electrical conductivity owing to the feeble ionization of a compound of the two acids.

The constitution of pyrophosphoric acid.—The analyses of T. Graham,[5] and E. M. Péligot established the empirical composition of pyrophosphoric acid, $H_4P_2O_7$. H. Giran found that the mol. wt. of a soln. of pyrophosphoric acid in glacial acetic acid decreases with time, and this the more the less the conc. of the soln. By extrapolation for zero time, he obtained the mol. wt. 534 corresponding with $(H_4P_2O_7)_3$. According to A. Holt and J. E. Myers, also, the f.p. of aq. soln. of the viscid, syrupy liquid, obtained by dehydrating the ortho-acid, is depressed in agreement with the assumption that the molecules of the acid are complex—between $(H_4P_2O_7)_4$ and $(H_4P_2O_7)_5$; while the soln. derived from the decomposition of the lead-salt contain the simple molecules $H_4P_2O_7$. The f.p. of freshly prepared soln. in acetic acid correspond with the mol. wt. $(H_4P_2O_7)_3$; and as time goes on, the mol. wt. diminishes to something between $(H_4P_2O_7)_2$ and $H_4P_2O_7$, which makes it appear as if in acetic acid soln., pyrophosphoric acid gradually depolymerizes. Strictly speaking, *orthodiphosphoric acid* should be $(HO)_4P.O.P(OH)_4$, represented by lead orthodiphosphate (*q.v.*), so that the ordinary acid is derived from this by the loss of 2 mols of water, furnishing probably $(HO)_2PO.O.PO(OH)_2$, which, in harmony with the nomenclature employed for the silicic acids—**6**. 40, 22—becomes *deuterodiphosphoric acid;* but this is commonly regarded as the ortho-acid. D. Balareff said that the molecule is probably not associated.

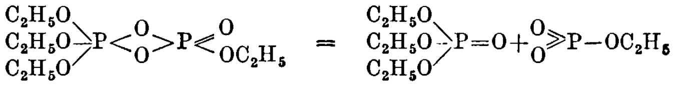
The heats of neutralization of pyrophosphoric acid with sodium hydroxide show that the acid is probably tetrabasic, for H. Giran found that the first two displaceable hydrogen atoms have strongly marked acidic functions, and the other two have feeble acidic functions. The graphic formula $(HO)_2{=}PO.O.PO{=}(OH)_2$ is in agreement with the tetrabasicity of the acid, and with the work of W. A. Tilden and R. E. Barnett. C. Favel also found pyrophosphoric acid behaved like a tetrabasic acid towards "soluble blue" indicator. The confident assumption that the phosphorus is quinquevalent precludes H. Wichelhaus' formula $(HO)_2P.O.O.O.P(OH)_2$; but, before the formula $(HO)_2PO.O.PO(OH)_2$ can be definitely accepted, it must be shown that the formulæ





are inadequate. The work of G. A. Abbott and W. C. Bray on the step-by-step ionization of the four hydrogen atoms of pyrophosphoric acid, indicated above, shows that the first two constants have nearly the same value, and are very different from the last pair of constants which are not very different from one another. This has been taken to mean that the four hydroxyl groups in the molecule of pyrophosphoric acid are related to one another in pairs, and that the formula of the acid is symmetrical, $(HO)_2PO.O.PO(OH)_2$ or $(HO)_2$ or $(HO)_2P{<}O_3{>}P(OH)_2$, and not asymmetrical, $(HO)_3P{<}O_2{>}PO.OH$. A. Geuther and A. Michaelis argued that since pyrophosphoryl chloride, $P_2O_3Cl_4$, yields orthophosphoric acid, not pyrophosphoric acid, when treated with water, the acid has probably the unsymmetrical formula $(HO)_3P{<}O_2{>}PO(OH)$. However, this argument loses its force when it is remembered that the heat of the reaction is so great that even if the pyro-acid were formed, it would be converted into the ortho-acid, owing to the consequent rise of temp. When the conditions of the reaction are such that it takes place slowly and less vigorously—say, by the action of moist air on pyrophosphoryl chloride, or of water on a dil. soln. of the chloride in carbon disulphide—pyrophosphoric acid is formed along with a little of the ortho-acid. Consequently, the formula of pyrophosphoric acid most probably depends on what formula best represents the constitution of pyrophosphoryl chloride (*q.v.*). D. Balareff said that the character of the ionization constants; the conditions of dehydration; the reaction with phosphorus pentachloride and sodium pyrophosphate in a sealed tube over 300°: $Na_4P_2O_7+3PCl_5=NaPO_3+3NaCl+4POCl_3$; the decomposition of $NaAg_3P_2O_7$ on fusion yielding Ag_3PO_4 and $NaPO_3$; and the formation of pyrophosphoric acid and metaphosphoric acid by the action of thionyl chloride on orthophosphoric acid, and the formation of pyrophosphoric acid alone when sulphuryl chloride is used, all favour the unsymmetrical formula.

Pyrophosphoric acid behaves like a monobasic acid when titrated with sodium hydroxide if cochineal be the indicator; and as a dibasic acid if Porrier's blue be the indicator. The tetrabasicity of pyrophosphoric acid is confirmed by the establishment of the molecular formula $(C_2H_5)_4P_2O_7$ for ethyl pyrophosphate, by J. Cavalier, by measuring its effect on the b.p. of benzene. When ethyl pyrophosphate is distilled, it breaks down into ethyl orthophosphate, $(C_2H_5)_3PO_4$, and probably ethyl metaphosphate, $C_2H_5PO_3$, which immediately decomposes into ethylene, C_2H_4, and metaphosphoric acid: $C_2H_5PO_3=C_2H_4+HPO_3$—the triethyl orthophosphate distils unchanged. The asymmetrical formula for pyrophosphoric acid explains this reaction very well:

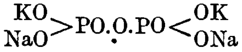


$$\begin{matrix}C_2H_5O\\C_2H_5O\\C_2H_5O\end{matrix}{>}P{<}\begin{matrix}O\\O\end{matrix}{>}P{<}\begin{matrix}O\\OC_2H_5\end{matrix} = \begin{matrix}C_2H_5O\\C_2H_5O\\C_2H_5O\end{matrix}{>}P{=}O+\begin{matrix}O\\O\end{matrix}{\gg}P-OC_2H_5$$

Similarly, A. Rosenheim and M. Pritze found that the raising of the b.p. of methyl or ethyl iodide by methyl pyrophosphate agrees with the mol. wt. of the methyl ester—between 239 and 264·5—and corresponds with the value 243 calculated for $(CH_3)_4P_2O_7$. Similarly for ethyl pyrophosphate.

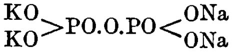
The pyrophosphates.—The pyrophosphates are prepared by mixing aq. soln. of the acid and base; by calcining a mol. of ortho- and meta-phosphoric acids with two mols. of a uniacid base, or the eq. of a polyacid base; and by heating, say, disodium hydrogen phosphate to 240°, or di-silver hydrogen phosphate to 170°, etc. J. H. Gladstone[6] found that many insoluble pyrophosphates are precipitated on metals, some of the precipitates form soluble double salts when treated with an excess of the soln. of sodium pyrophosphate—*e.g.* iron, copper, mercurous, zinc, cobalt, nickel, manganese, uranium, and aluminium pyrophosphates —but not mercuric or chromic salts; the addition of sulphuric acid to the soln. of the double salt may give a precipitate which re-dissolves in the dil. acid soln.; and treatment of the soln. of the double pyrophosphate with ammonium sulphide precipitates the sulphides of zinc, cobalt, nickel, and iron, but not manganese, uranium, chromium, or aluminium.

Curiously enough, tetrabasic pyrophosphoric acid readily forms *quaternary* or normal pyrophosphates, say $Na_4P_2O_7$, etc.; and the *secondary* pyrophosphates, say $Na_2H_2P_2O_7$, but not the primary and tertiary salts. There is even some doubt if the ternary salt, $Na_3HP_2O_7$, and the primary salt, $NaH_3P_2O_7$, have been prepared. T. Salzer reported the former in 1894; and H. Giran, the latter in 1903. Abortive attempts have been made to prepare a pair of isomeric potassium sodium pyrophosphates:



$$\begin{matrix}KO\\NaO\end{matrix}{>}PO.O.PO{<}\begin{matrix}OK\\ONa\end{matrix}$$

Symmetrical.



$$\begin{matrix}KO\\KO\end{matrix}{>}PO.O.PO{<}\begin{matrix}ONa\\ONa\end{matrix}$$

Asymmetrical.

the first by calcining potassium sodium orthophosphate, and the second by calcining a mixture of dipotassium and disodium orthophosphates:

$$\begin{matrix}KO\\NaO\end{matrix}{>}PO-\boxed{OH\ H}O-PO{<}\begin{matrix}OK\\ONa\end{matrix}$$

$$\begin{matrix}KO\\KO\end{matrix}{>}PO-\boxed{OH\ H}O-PO{<}\begin{matrix}ONa\\ONa\end{matrix}$$

Pyrophosphoric acid, said A. B. Poggiale, is not poisonous in dil. soln. and M. Paquelin and L. Jolly said that the pyrophosphates pass through the system unchanged but act as diuretics. The quaternary salts, $M_4P_2O_7$, are not changed by heat unless they are salts of the metals whose oxides are readily decomposed by heating; the secondary salts, $M_2H_2P_2O_7$, form metaphosphates and water; all the pyrophosphates are converted into orthophosphates when heated with alkali hydroxides or carbonates: $M_4P_2O_7+M_2O \rightarrow 2M_3PO_4$. H. Struve found that the pyrophosphates of the metals whose oxides are reduced when heated with **hydrogen** are decomposed when heated with this gas, forming the metal phosphide, orthophosphoric acid, and water; pyrophosphates of the metals whose oxides are not reduced when heated with hydrogen form orthophosphates, phosphorous oxide, and sometimes also phosphine, and a little red phosphorus; the pyrophosphates of the metals whose oxides are reduced by heat alone form orthophosphates, the metal, water, etc., when heated with hydrogen. H. Rose says that aq. soln. of the alkali pyrophosphates are not changed either by standing for a long time, or by boiling with **water**; J. H. Gladstone also said that the quaternary pyrophosphates are not changed by boiling with water or neutral salt soln.; but A. Reynoso found that by heating them with water to 280°, they are changed into secondary orthophosphates if they give an insoluble orthophosphate; and into a primary orthophosphate—*vide supra* for the hydration of pyrophosphoric acid. The secondary salts react feebly acidic with both litmus and phenolphthalein, but neutral with methyl-orange. The normal or quaternary alkali pyrophosphates are soluble in water, and the aq. soln. has a feeble alkaline reaction. T. Salzer said that the **halogens** react with an aq. soln. of sodium pyrophosphate, forming sodium bromide, hypobromite, and hydropyrophosphate, leaving much pyrophosphate unattacked. When boiled with **acids,** say sulphuric acid, R. Weber found that the pyrophosphates are transformed into the ortho-salts, but the pyrophosphates were found by E. F. Smith and J. G. Gibbs not to be attacked by **hydrogen chloride.** According to H. Rose, the pyrophosphates are transformed into orthophosphates by fusion with **alkali carbonates.** H. Girard formed orthophosphoric acid and sodium thiosulphate with the evolution of hydrogen sulphide by boiling aq. soln. of sodium pyrophosphate with flowers of **sulphur.** T. Salzer stated that no orthophosphoric acid is formed, but the reaction occurs in the sense of the equation: $x\mathrm{Na_4P_2O_7}+12\mathrm{S}+3\mathrm{H_2O}=2\mathrm{Na_2S_5}+\mathrm{Na_2S_2O_3}+6\mathrm{Na_3HP_2O_7}+(x-6)\mathrm{Na_4P_2O_7}$, where x depends on the conc., temp., and press. G. Buchner found that **ammonium sulphide** precipitates zinc, cobalt, nickel, and iron, but not manganese, uranium, or chromium from soln. of the double pyrophosphates. The action of the **phosphorus chlorides** is not to chlorinate pyrophosphoric acid to pyrophosphoryl chloride, $\mathrm{P_2O_3Cl_4}$—as might be expected: $\mathrm{H_4P_2O_7}+\mathrm{PCl_5}=\mathrm{H_3PO_4}+\mathrm{P_2O_3Cl_4}+\mathrm{HCl}$—but rather to dehydrate the pyro- to the meta-acid, thus, when pyrophosphoric acid is heated with **phosphorus pentachloride,** $\mathrm{PCl_5}$, A. Geuther showed that it forms phosphoryl chloride: $\mathrm{H_4P_2O_7}+\mathrm{PCl_5}=2\mathrm{HPO_3}+\mathrm{POCl_3}+2\mathrm{HCl}$, or in the extreme case: $\mathrm{H_4P_2O_7}+5\mathrm{PCl_5}\rightarrow 4\mathrm{HCl}+7\mathrm{POCl_3}$—it may be that pyrophosphoryl chloride is first formed, and subsequently breaks down to phosphoryl chloride by a secondary reaction: $2\mathrm{P_2O_3Cl_4}+2\mathrm{PCl_5}\rightarrow 6\mathrm{POCl_3}$; pyrophosphoric acid also reacts slowly with **phosphoryl chloride**: $2\mathrm{H_4P_2O_7}+\mathrm{POCl_3}=5\mathrm{HPO_3}+3\mathrm{HCl}$; and with **phosphorus trichloride,** $\mathrm{PCl_3}$, it forms metaphosphoric and phosphorous acids: $\mathrm{PCl_3}+3\mathrm{H_4P_2O_7}=6\mathrm{HPO_3}+\mathrm{H_3PO_3}+3\mathrm{HCl}$; similar remarks apply to the action of **thionyl chloride,** $\mathrm{H_4P_2O_7}+\mathrm{SOCl_2}\rightarrow 2\mathrm{HPO_3}+\mathrm{SO_2}+2\mathrm{HCl}$. P. de Clermont prepared **tetraethyl pyrophosphate,** $\mathrm{(C_2H_5)_4P_2O_7}$, by the action of ethyl iodide, $\mathrm{C_2H_5I}$, on silver pyrophosphate, $\mathrm{Ag_4P_2O_7}$, at 100°. The liquid has a sp. gr. 1·17 at 17°; it is soluble in water and alcohol; it decomposes when heated; and it forms with potash-lye, **diethyl potassium orthophosphate,** $\mathrm{K(C_2H_5)_2PO_4}$. W. W. Worms, and A. A. Panormoff studied the soluble compounds pyrophosphoric acid forms with **albumen.** The aq. soln. of the pyrophosphates give a white precipitate with soln. of **silver nitrate,** and with **barium or calcium chloride.** According to J. L. Lassaigne, these reactions are so sensitive that a strong turbidity is produced with soln. containing one part of the acid in 10,000 parts of water; a faint turbidity with 1 : 20,000; and very faint with 1 : 40,000—that with the calcium salt appears only in about half an hour; with 1 : 80,000, the calcium salt gives no turbidity, the other salts give a faint cloudiness; and with 1 : 160,000, a faint opalescence. W. Gibbs observed that pyrophosphoric acid forms complexes with **tungstic acid.**

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[2] E. B. R. Prideaux, *Chem. News*, **99.** 161, 1909; E. Giana, *German Pat., D.R.P.* 219680,

§ 26. Metaphosphoric Acid

J. J. Berzelius[1] showed that when ordinary phosphoric acid is calcined, the product is fundamentally different from orthophosphoric acid in that it has acquired the power of coagulating a soln. of albumen. The same product is obtained by the action of a small proportion of water on phosphorus pentoxide; and H. Giran said that the main product of the first action is metaphosphoric acid. E. B. R. Prideaux noted that 75 per cent. of metaphosphoric acid is formed during the dissolution of phosphoric pentoxide in an excess of water at room temp.—the remainder is orthophosphoric acid. T. Graham further showed that by gradually heating sodium dihydrogen or diammonium phosphate, three different salts can be obtained, and he investigated the properties of the product which appears as a vitreous or glassy mass and which, for a time, was named *Graham's salt;* it has the empirical composition $NaPO_3$, sodium monometaphosphate: $Na(NH_4)_2PO_4=H_2O+2NH_3+NaPO_3$. T. Graham says that the syrupy acid is preferably heated in a gold crucible since other metals, including platinum, are attacked. The aq. soln. of the cold mass when treated with lead nitrate furnishes a precipitate of the lead salt, $Pb(PO_3)_2$; when the washed precipitate, suspended in water, is treated with hydrogen sulphide, lead sulphide is precipitated. The excess of hydrogen sulphide is driven from the aq. soln. by a current of air, and a soln. of metaphosphoric acid remains. W. Gregory, R. Maddrell, A. Joly, etc., prepared the acid by calcining orthophosphoric acid to 316°, and they considered pyrophosphoric acid to be an intermediate product of the transformation. A. Joly

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also prepared the meta-acid by the action of heat on pyrophosphoric acid; G. Watson says the conversion occurs between 290° and 300°; and G. Tammann, that the transformation occurs when the ortho-acid is heated beyond the point where it begins to fume. A. Besson obtained metaphosphoric acid by heating ammonium hydrophosphate, $(NH_4)_2HPO_4$. Metaphosphoric acid was prepared by A. Besson, by the action of hydriodic acid on phosphoryl chloride; G. Gustavson, by heating iodine or bromine with orthophosphorous acid, H_3PO_3, in a sealed tube at 100°: $2H_3PO_3+2Br_2=4HBr+2HPO_3$; if a smaller proportion of bromine be used, the ortho-acid is formed: $4H_3PO_3+3Br_2=3HBr+PBr_3+3H_3PO_4$. O. Ordinaire, however, obtained monobromophosphorous acid by heating two gram-molecules of bromine with one of phosphorous acid. A. Geuther obtained metaphosphoric acid by the action of an excess of phosphoryl chloride on orthophosphoric acid: $3H_3PO_4+PCl_3=3HPO_3+H_3PO_3+3HCl$; phosphorous chloride gave a similar result: $2H_3PO_4+POCl_3=3HPO_3+3HCl$. C. F. Gerhardt found the meta-acid to be produced by heating moist phosphamide or phospham in the absence of air: $HPN_2+3H_2O=2NH_3+HPO_3$. H. Schiff also found it to be produced when phosphoryl chloride acts upon salicylic or other polybasic acids.

Some physical properties of metaphosphoric acid.—Metaphosphoric acid is a transparent, vitreous solid sometimes called *glacial phosphoric acid.* E. Brescius[2] said that the glacial acid is soft and flexible, and the presence of sodium phosphate makes it hard. The commercial acid is sold in sticks, and, according to A. Bettendorff, it often contains some sodium salts and some ortho- and pyro-acids as impurities. The dry acid deliquesces rapidly in air, and it readily dissolves in water with the development of much heat. The acid solidifies to a vitreous mass without crystallization from solutions with less than 63 per cent. of water. P. Harting says that one part of the acid in 10,000 parts of water reddens blue litmus. According to H. Rose, metaphosphoric acid volatilizes at a bright red-heat, and is not dehydrated further than $(HPO_3)_n$ by heat or by dehydrating agents, although W. A. Tilden and R. E. Barnett find that at a high temperature there are signs of the loss of a little water because the product contained rather more phosphoric anhydride than corresponds with the formula HPO_3. H. Giran did not succeed in obtaining a f.p. curve of mixtures of the meta-acid and water because of the formation of vitreous glasses. F. M. Raoult, and E. Cornec measured the **lowering of the freezing point** of aq. soln. of metaphosphoric acid and obtained results in agreement with a polymerized molecule. According to H. Giran, the **heat of formation** is $(H,P,3O)=HPO_{3\text{solid}}+$between 224·88 and 226·61 Cals. and $(H,P,3O)=HPO_{3\text{aq.}}+236{\cdot}37$ Cals. H. Giran gives for the **heat of solution** of the solid acid 9·76 Cals., while A. Joly gives 4·63 Cals. The **heat of neutralization** of a mol. of potassium hydroxide, by water sat. with metaphosphoric acid, is 325·4 units; similarly, for sodium hydroxide, 474·4 units. J. Thomsen obtained: $2HPO_{3\text{aq.}}+NaOH_{\text{aq.}}=14{\cdot}4$ Cals.; and $2HPO_{3\text{aq.}}+2NaOH_{\text{aq.}}=28{\cdot}75$ Cals. H. Giran found $NaOH_{\text{aq.}}+HPO_{3\text{aq.}}=14{\cdot}84$ Cals., and $NaOH_{\text{solid}}+HPO_{3\text{solid}}=63{\cdot}03$ Cals.; he also gives 10·22 Cals. for the **heat of transformation** of HPO_3 with H_3PO_4. J. H. Gladstone gives 18·68 for the **refraction equivalent,** and, for the **index of refraction** of a soln. in 8·23 eq. of water (sp. gr. 1·270) at 20·5°, 1·3718 for the *A*-linc, 1·3764 for the *D*-line, and 1·3879 for the *H*-line. F. Zecchini has studied the molecular refraction of the metaphosphates; and A. Kundt, the double refraction—C. Zakrewsky and G. Kraft found that the optical behaviour of the acid is like that of an oil. W. W. Coblentz found metaphosphoric acid to be too opaque to give other than an imperfect **ultra-red transmission spectrum.**

G. Janecek[3] observed that spontaneously inflammable phosphine is evolved during the electrolysis of solutions of the metaphosphates. S. Arrhenius, in his thesis *Recherches sur le conductibilité galvanique des electrolytes* (Stockholm, 1884), gave measurements of the electrical resistance, and the **electrical conductivity** of the acid. E. B. R. Prideaux found the meta-acid has a greater conductivity than the ortho-acid; while A. Holt and J. E. Myers found the meta-acid to be slightly ionized in aq. soln. Starting with an acid containing about 75 per cent. of metaphosphoric acid and 25 per cent. of orthophosphoric acid, E. B. R. Prideaux found that the electrical conductivity for the first 20 hrs. suffers but little change; it then decreases in accord with an exponential law for about 160 hrs., and thereafter decreases at a rather slower rate as illustrated by Fig. 48. The alteration is attended by a change from polymerized $(HPO_3)_n$ to simple HPO_3 mols, the former being a bad conductor; the polymerization of the $(HPO_3)_n$-acid attended by a hydration of the HPO_3-acid to H_3PO_4, the former change being probably the quicker. Fig. 47 shows the sp. conductivity of the acid for different conc. at 18° and at 25° of the mixed acids. The actual conductivity of the simple metaphosphoric acid alone is unknown, since the aq. soln. always contains the polymerized acid and orthophosphoric acid as well. When the hydration is complete, the conductivities of the soln. correspond with those required for orthophosphoric acid. Starting from the right, the curves, Fig. 48, show that the conductivity increases only slightly with the change in the conc. of the soln. This is presumably due to the presence of the polymerized, non-conducting molecules. It is then inferred that the lower part of the curves represents the relation between conductivities and conc. of simple molecules HPO_3 and H_3PO_4. If the curve is continued on this assumption, the point where it strikes the ordinate from 240 millimols per litre represents the theoretical conductivity of HPO_3. The conductivity so found is 544 at 18° and 590 at 25°, the percentage increase for 1° being 1·2, as in soln. of partly changed HPO_3. If this represents the conductivity of non-polymerized HPO_3, it is interesting to notice that it is of the same order as that of iodic acid at 250 millimols per litre, namely, 573. W. Hittorf found the transport number of the anion of normal sodium metaphosphate to be 0·573; and A. Wicsler, 0·590.

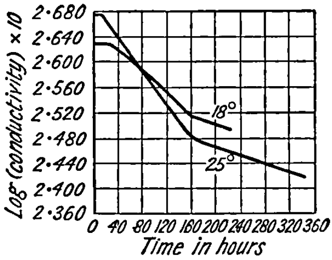


FIG. 47.—The Change of the Electrical Conductivity of Metaphosphoric Acid Solutions with Time.

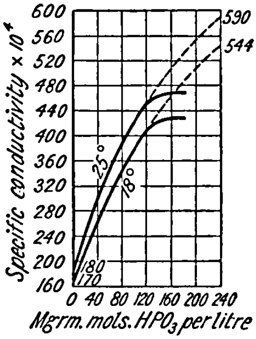


FIG. 48.—The Electrical Conductivity of Solutions of Metaphosphoric Acid.

The hydration of metaphosphoric acid.—The aq. soln. of metaphosphoric acid was found by T. Graham[4] to pass slowly into the ortho-acid, but not into the pyro-acid; the change is accelerated by boiling the soln., or by treating it with acids. According to A. Vogel, the change of meta- to the ortho-acid, in aq. soln., is not accompanied by any change in vol.; and C. Montemartini and U. Egidi found the reaction is unimolecular: $HPO_3+H_2O=H_3PO_4$. The velocity of transformation is faster the greater the concentration of the metaphosphoric acid in soln. J. C. and F. C. Blake did not find the reaction to be proportional to the amount of unchanged substance left in the soln., and H. Giran found the speed of hydration of metaphosphoric acid to be faster than that of the pyro-acid, and that the reaction is too complex to be represented by a simple equation. This latter result was also obtained by A. Holt and J. E. Myers. The speed of the reaction is very sensitive to variations of temp. Thus, P. Sabatier found that a

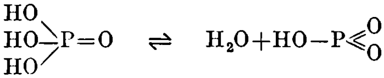
$\frac{1}{2}N$-soln. required 150 days for complete conversion to the ortho-acid at 0°, it required but 5 days at 31°, and less than an hour at 95°. P. Sabatier also found that the presence of a strong mineral acid, like sulphuric or hydrochloric acid, accelerates the change, while a weak organic acid, like acetic acid, retards the conversion; he further proved that the transformation is arrested if the metaphosphoric acid be completely neutralized by a strong base like sodium hydroxide, for, at 0° no change was observed, and only a slight formation of the ortho-salt at 43·5°. With the protracted boiling of the soln. the meta-salt was completely transformed into the ortho-salt; if the meta-acid be incompletely neutralized the transformation is slower than with the free acid, and faster than with the completely neutralized acid; while if some alkali be in excess, the transformation is rather slower than with the completely neutralized acid.

There have been some differences of opinion as to whether the meta-acid is hydrated directly into the ortho-acid, or whether it passes *viâ* the pyro-acid as an intermediate stage. T. Graham, J. M. Maisch, P. Sabatier, C. Montemartini and U. Egidi, and D. Balareff supposed the change to be direct; while M. Berthelot and G. André, S. Tanatar, and H. Giran considered the pyro-acid to be formed as an intermediate product. It is known that the dehydration of the ortho-acid produces first the pyro-acid and then the meta-acid; and it might be expected that the rehydration of the meta-acid would take place in the reverse manner. The trouble has arisen from the difficulties in detecting the pyro-acid in the presence of the meta- and ortho-acids; and, on account of the polymerization of the different acids in aq. soln., physical methods of testing the hypothesis give ambiguous results. A. Holt and J. E. Myers were able to demonstrate the intermediate formation of the pyro-acid in the hydration of the meta- and the ortho-acid by the fractional precipitation of the soln. by adding silver nitrate in small portions at a time, and filtering off the resulting precipitates one by one. At first yellow silver ortho-phosphate separates, and afterwards a colourless precipitate is obtained—the absence of colour shows that the precipitate is either silver pyro- or meta-phosphate. When the precipitate is washed and treated with hydrochloric acid to precipitate the silver, a soln. is obtained which does not coagulate albumen, showing the absence of metaphosphoric acid. The accumulation of the pyro-acid in the soln. shows that the passage from the meta- to the pyro-acid is faster than the change from the pyro- to the ortho-acid. Again, the transformation of meta- to ortho-phosphoric acid is faster the more conc. the soln., and the higher the temp.—*e.g.* the transformation of a $\frac{1}{2}N$-soln. at 0° occupies about 150 days; at 31°, about 5 days; and at 95°, less than half an hour. The presence of strong mineral acids—sulphuric or hydrochloric acid—accelerates the change; while the weak acids—acetic acid—retards the speed of conversion; the presence of alkalies also retards the change. L. Pessel found that $H^{\cdot}$-ions accelerate the rate of hydration; that the velocity constant increased with time owing to the polymerization of the metaphosphoric acid; that pyrophosphoric acid is not formed as an intermediate compound in the process; and, as pointed out by P. Sabatier, the conversion of sodium metaphosphate to orthophosphate is accelerated by an excess of alkali.

Four varieties of metaphosphoric acid have been reported. (i) The meta-acid, prepared by heating commercially pure glacial phosphoric acid for a short time to redness, furnishes a glassy solid which is deliquescent in moist air, and quickly dissolves in water to form a soln. whose f.p. corresponds with the presence of molecules, $(HPO_3)_3$; T. Graham's soluble salt, sodium metaphosphate, in aq. soln. also has a mol. wt. corresponding with $(NaPO_3)_3$. (ii) If the preceding variety of the meta-acid be heated for several hours to redness, it forms a brittle glass with a sp. gr. 2·488. This is less deliquescent in moist air than the former modification, and, when placed in water, it appears to decrepitate, minute particles being shot into the liquid so as to form a turbid soln. (iii) When this crackling variety is heated for about 24 hrs. at a dull red-heat, it forms a brittle glass with a sp. gr.

2·216; this form of the acid does not deliquesce, unless perhaps very slowly, and it dissolves very slowly in water. The dissolution in water is not attended by any crackling phenomenon as is the case with the preceding variety. F.p. determinations indicate that the soln. contains molecules of $(HPO_3)_2$. (iv) According to A. Holt and J. E. Myers, aq. soln. of the acid prepared by decomposing lead metaphosphate have a f.p. in agreement with a soln. of mol. wt. HPO_3. E. Cornec has shown that the mol. wt. of metaphosphoric acid in water, and others, in acetic acid soln., varies with time presumably because the acid becomes complex.

Analyses of metaphosphoric acid, by E. M. Péligot, R. Weber, P. L. Dulong, H. Rose, and W. A. Tilden and R. E. Barnett, agree with the empirical formula HPO_3. That by C. L. Berthollet is more like pyrophosphoric acid. W. A. Tilden and R. E. Barnett showed that the mol. wt. of metaphosphoric acid when in a state of vapour at a bright red-heat is 76·8, and 78·2 when the theoretical value for $(HPO_3)_2$ is 80—hence the vapour is a bimolecular complex, $(HPO_3)_2$, which shows signs of dissociation at elevated temp., and parts with a little water. Hence, the meta-acid may be related to the pyro-acid as $HO{-}PO{=}O_2{=}PO{-}OH$ and $(HO)_2{=}PO{-}O{-}PO{=}(OH)_2$. The ordinary method of representing the dehydration of the ortho-acid is:



$$\begin{matrix}\mathrm{HO}\\ \mathrm{HO}\\ \mathrm{HO}\end{matrix}{>}\mathrm{P{=}O} \rightleftharpoons \mathrm{H_2O+HO{-}P}{\lessgtr}^{\mathrm{O}}_{\mathrm{O}}$$

which favours the idea that metaphosphoric acid bears the same relation to phosphorus that nitric acid bears to nitrogen. H. Giran found the mol. wt. in glacial acetic acid soln. decreases with time, and approximates to a limiting value 400 for zero time—this agrees with the formula $(HPO_3)_5$—and the limiting value is smaller the more dil. the soln. E. B. R. Prideaux also found the soln. to contain simple and polymerized molecules. According to A. Hantzsch, metaphosphoric acid in conc. sulphuric acid soln. behaves as if it were split into two ions.

The chemical properties of metaphosphoric acid.—A. B. Poggiale[5] said that the dil. aq. soln. of the acid is not poisonous, and that the conc. soln. acts like other strong acids. O. Schulz found that subcutaneous injections in rabbits had a toxic action. J. J. Berzelius found that metaphosphoric acid deliquesces rapidly when exposed to **air**; and dissolves in **water** with the development of much heat. When water is poured over the glacial acid, the mass splits with violence into small pieces, some of which are projected upwards. Dissolution occurs only slowly. The action of water has been already discussed. Owing to the probable fact that solid metaphosphoric acid is polymerized and that when dissolved in water depolymerization and hydration simultaneously occur, the reported properties—physical and chemical—of this acid are affected accordingly. P. Harting said that one part of the acid in 10,000 parts of water will redden blue litmus. H. Giran attempted to determine the solubility curve of metaphosphoric acid in water as he did for the ortho- and pyro-acids, but he found that the soln. of the meta-acid froze to vitreous glasses, and did not crystallize. D. Balareff observed that an aq. soln. of metaphosphoric acid slowly forms orthophosphoric acid on keeping. According to T. Fleitmann, and G. von Knorre, the *monometaphosphates* are usually very sparingly soluble in water, so that, as T. Graham noted, **potassium hydroxide** precipitates from the aq. soln. Not one of the three acids—ortho-, pyro-, or meta- —is changed by hydrogen, although W. A. Ross found that when metaphosphoric acid is heated with **zinc**, phosphine is formed; when heated with **aluminium,** L. Frank found that an aluminate, aluminium phosphide, and phosphorus are formed; when the acid is heated with **carbon,** W. Neumann noted that phosphorus is set free; when heated with **silica,** P. Hautefeuille and J. Margottet, and K. Hüttner obtained the complex $P_2O_5.SiO_2$. W. Gibbs also obtained complexes with **molybdic acid** and with **tungstic acid**. A. Geuther found that when warmed with **phosphorus pentachloride,** metaphosphoric acid reacts $HPO_3+2PCl_5=3POCl_3+HCl$; while **phosphoryl chloride** and **phosphorus trichloride** have no action. C. F. Schönbein found when melted with **iodides,** the reaction is violent, iodine and hydrogen iodide being given off. J. Heimann found that metaphosphoric acid does not dissolve in hydrocarbons; it dissolves in all proportions in **acetic anhydride,** in **benzaldehyde, benzophenone,** and other organic **anhydrides, aldehydes,** and **ketones.** He also found that **zinc, lead, tin, iron, copper,** and **silver** are dissolved by soln. of metaphosphoric acid, while **platinum** is not attacked. The electrochemical series is in the order named. W. Schlömann found that a freshly prepared conc. soln. gives a precipitate with an alcoholic or ethereal soln. of the **primary mono-** or **di-amines,** but not with the **secondary** or **tertiary amines.** R. Lorenz found that metaphosphoric acid forms a compound with **gluten.**

Aq. soln. of the pyrophosphates give a white crystalline precipitate with **silver nitrate**—orthophosphates give a yellow precipitate, and metaphosphates give a white gelatinous precipitate—all three precipitates are soluble in ammonia, and in nitric acid, so that the precipitate is formed only in neutral soln. The pyrophosphates give a white earthy precipitate with **barium or calcium chloride or nitrate** provided the soln. is not acidic—similar results are obtained with the ortho- and the meta-phosphates. All three precipitates are soluble in acids—even acetic acid—and hence differ from ferric and aluminium phosphates. Ammonia re-precipitates the phosphate from the soln. in acids. These salts have been also studied by C. Hindenlang, G. Denigés, and F. Warschauer. According to P. Harting, precipitates can be obtained with calcium or lead salts from soln. of one part of pyrophosphoric acid in 10,000 parts of water, or in 20,000 parts of water if the mixture is allowed to stand for half an hour. **Magnesium chloride** gives a white precipitate with pyrophosphates—the precipitate is soluble in an excess of the pyrophosphate or magnesium salt; moderately dil. soln. of the metaphosphates give no such precipitate, and orthophosphates give a precipitate in the presence of ammonium chloride and ammonia. A soln. of **albumen** and acetic acid gives no precipitate with pyrophosphates—alkalies should be absent since alkali acetates give precipitates even in the absence of albumen. The alkali metaphosphates do not coagulate albumen, but free metaphosphoric does do so. **Ammonium molybdate** gives no precipitate in the cold with nitric acid soln. of meta- and pyro-phosphates, but the ortho-phosphates give a yellow crystalline precipitate of ammonium phosphomolybdate: $H_3PO_4+12(NH_4)_2MoO_4+21HNO_3=(NH_4)_3PO_4.12MoO_3+21NH_4NO_3+12H_2O$; the yellow precipitate is readily soluble in ammonia, alkali-lees, and in an excess of a soln. of alkali phosphate; and compounds are formed containing less molybdenum than is represented by this equation. Hence, in the gravimetric determination of phosphates by this reaction, it is necessary to employ a large excess of the ammonium molybdate soln. to prevent the formation of a precipitate low in molybdenum. If the meta- or pyro-phosphates are boiled with the ammonium molybdate, the yellow precipitate is formed because the meta- and pyro-phosphates are changed into the ortho-salt. According to C. D. Braun,[6] luteocobalt chloride, or **cobaltic sodium hexamminopyrophosphate,** when added drop by drop to a soln. of an alkali pyrophosphate (neutralized with an alkali), forms a reddish-yellow crystalline precipitate resembling lead iodide, and which, according to S. M. Jörgensen, has the composition, $[Co(NH_3)_6]NaP_2O_7.11\frac{1}{2}H_2O$. If metaphosphates be present, some may be carried down mechanically with the precipitated pyrophosphate, otherwise the reaction could be applied quantitatively. Alkali salts of the ortho- and metaphosphates do not give precipitates with the luteocobalt chloride unless the mixture has stood for some hours, and even then the precipitates are readily distinguished from that with a pyrophosphate. The more important distinguishing tests for the three acids or acidic soln. of the salts of the acids are summarized in Table VII. The reactions with silver nitrate, barium chloride or nitrate, and albumen are the more important.

Table VII.—Some Reactions of the Phosphoric Acids.

——	Orthophosphoric acid.	Pyrophosphoric acid.	Metaphosphoric acid.
Silver nitrate . . .	Yellow pp.	White cryst. pp.	White gel.
Barium chloride . .	No pp. In alkaline soln. white pp.	No pp. In alkaline soln. white pp.	White pp.
Albumen . . .	Nil.	Nil.	White pp.
Zinc acetate . . .	Nil.	White pp.	Nil.
Ammonium molybdate in nitric acid	Citron-yellow pp.	Nil.	Nil.
Luteocobalt chloride .	No immediate pp.	Reddish-yellow pp.	No immediate pp.
Aluminium salts . .	Pp. soluble in acetic acid.	Pp. insoluble in acetic acid.	Pp. insoluble in acetic acid.
Chromium salts . .	Ibid.	Ibid.	Ibid.
Cobalt salts . . .	Blue; soluble in acetic acid.	Red; insoluble in acetic acid.	Red; insoluble in acetic acid.
Bismuth salts in alkaline soln.	Nil.	Nil.	White pp.

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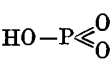
§ 27. The Polymetaphosphoric Acids and their Salts

Metaphosphoric acid forms a number of salts which have the same percentage composition—one equivalent of monobasic acid to one of mono-acid base—but, when prepared in different ways their properties are so different that it does not appear likely that they can be referred to the same parent acid. The nature of these differences is not very clear; and E. Cornec[1] said that *ces sels constituent un des chapitres obscurs de la chimie minérale.* T. Fleitmann regarded the differences as the result of different polymerized forms of the monobasic acid, and he postulated a series of metaphosphoric acids formed by the union of 1, 2, 3, . . . mols. of water with 1, 2, 3, . . . mols. of phosphoric anhydride—*e.g.* monometaphosphoric acid: $H_2O+P_2O_5=H_2P_2O_6$, or $(HPO_3)_2$; $2H_2O+2P_2O_5=H_4P_4O_{12}$, or $(HPO_3)_4$; etc. The polymetaphosphoric acids can be regarded as forming a series of homologues with the general formula: $mH_3PO_4—mH_2O$, or $(HPO_3)_n$, where m ranges from 1 to 5, or even to 8, 10, and 14.

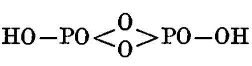
HPO_3, Monometaphosphoric acid.	$NaPO_3$, Sodium metaphosphate.
$(HPO_3)_2$, Dimetaphosphoric acid.	$K_2P_2O_6$, Potassium dimetaphosphate.
$(HPO_3)_3$, Trimetaphosphoric acid.	$Na_3P_3O_9$, Sodium trimetaphosphate.
$(HPO_3)_4$, Tetrametaphosphoric acid.	$Pb_2P_4O_{12}$, Lead tetrametaphosphate.
$(HPO_3)_4$, Pentametaphosphoric acid.	$(NH_4)_5P_5P_{15}$, Ammonium pentametaphosphate.
$(HPO_3)_6$, Hexametaphosphoric acid.	$Na_6P_6O_{18}$, Sodium hexametaphosphate.

The graphic formulæ for the parent acids may be represented in at least two ways:



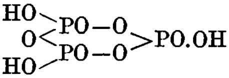
$$HO-P\begin{smallmatrix}\lessgtr\end{smallmatrix}^{O}_{O}$$

Monometa-
phosphoric acid.



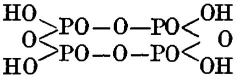
$$HO-PO<^{O}_{O}>PO-OH$$

Dimetaphosphoric
acid.



$$\begin{matrix}HO\searrow & PO-O & \\ O< & & >PO.OH \\ HO\nearrow & PO-O & \end{matrix}$$

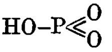
Trimetaphosphoric
acid.



$$\begin{matrix}HO\searrow & PO-O-PO<^{OH} \\ O\lessgtr & \quad\quad\quad O \\ HO\nearrow & PO-O-PO<_{OH}\end{matrix}$$

Tetrametaphosphoric
acid.

Again, by adding tervalent groups —O.PO= to the phosphorus atom of metaphosphoric acid, graphic formulæ for the more complex metaphosphoric acids can be obtained:

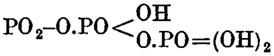


$$HO-P\begin{smallmatrix}\lessgtr\end{smallmatrix}^{O}_{O}$$

Monometa-
phosphoric acid.

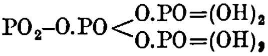
$$PO_2-OPO<^{OH}_{OH}$$

Dimetaphosphoric
acid.



$$PO_2-O.PO<^{OH}_{O.PO=(OH)_2}$$

Trimetaphosphoric
acid.



$$PO_2-O.PO<^{O.PO=(OH)_2}_{O.PO=(OH)_2}$$

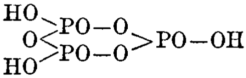
Tetrametaphosphoric
acid.

There is no definite evidence in favour of these or indeed of other possible explanations of the constitution of these acids. Indeed, the evidence as to their chemical individuality is not above suspicion. Only the salts, not the acids, are known.

Monometaphosphates.—By heating microcosmic salt, $(NH_4)NaHPO_4$, on a gradually rising temp., T. Fleitmann and W. Henneberg, obtained results similar to those previously obtained by T. Graham, first disodium dihydrogen pyrophosphate, and then a vitreous cake, which, when treated with an excess of water formed what are called *Graham's soluble salt* and *Graham's insoluble salt*—both are modifications of sodium metaphosphate. T. Fleitmann and W. Henneberg separated what they considered to be sodium trimetaphosphate from the soluble portion; while the insoluble part—called *Maddrell's insoluble salt*—was supposed to be sodium monometaphosphate. A similar salt was prepared by R. Maddrell from alkali nitrate and phosphoric acid; and the same salt is supposed to be generally obtained by heating an alkali oxide with an eq. amount of phosphoric acid to a red-heat (but not high enough to melt the mass) until the residue does not give an acid reaction. The portion which remains when the product is leached with water is supposed to be the salt in question. T. Fleitmann was unable to make any double salts with the monometaphosphate. It is not yet proved that the constitution of these salts is really that postulated by T. Fleitmann and W. Henneberg. When the sodium salt is digested for some weeks with a soln. of potassium or ammonium chloride, it furnishes the corresponding potassium or ammonium salt—$2KPO_3.3H_2O$, or $5NH_4PO_3.6H_2O$. According to G. Tammann, these salts may be regarded as α-**monometaphosphates,** another isomeric series of monometaphosphates is formed by neutralizing a soln. of metaphosphoric acid with alkali carbonate, whereupon $Na_2HPO_4.12H_2O$ separates, and the mother-liquid, at 50°, furnishes microscopic crystals of what G. Tammann called β-**monometaphosphate,** which when compressed and dried on earthenware slabs have a composition corresponding with $NaPO_3.1\frac{1}{2}H_2O$. When moist, this salt quickly passes into the orthophosphate. Potassium and ammonium monometaphosphates are formed in a similar manner. If R. Maddrell's insoluble salt be heated to redness, it melts to a colourless fluid, which, on cooling, forms a transparent glass—*Graham's salt.* For the preparation of an aq. soln. of monometaphosphoric acid, *vide supra.* P. Pascal argued that the salts and acids formed at a high temp. are highly polymerized, and he prepared the monometaphosphate by the action of ethyl hexametaphosphate on sodium ethoxide in alcoholic soln. The reaction is violent, and yields a yellow, sticky mass: $(C_2H_5PO_3)_6+6C_2H_5ONa=6(C_2H_5)_2NaPO_4$; and $(C_2H_5)_2NaPO_4=NaPO_3+(C_2H_5)_2O$. When washed with warm alcohol, the sodium salt obtained in a 30–40 per cent. yield is in the form of small, colourless, deliquescent grains. Its neutral soln. gives white salts with lead, silver, and barium salts; leuteocobalt chloride gives no reaction for pyrophosphates; its soln. in acetic acid coagulates albumen. The f.p. method shows that its mol. wt. is in agreement with $NaPO_3$, and is the same as that prepared at 250°, and 300°. P. Pascal found that the insoluble alkali monometaphosphates of T. Graham, and R. Maddrell are soluble in soln. of the pyrophosphates, even $0{\cdot}1N$-soln., and they are really complexes of high mol. wt. Only the salts prepared by P. Pascal at a low temp. are truly monometaphosphates. J. Müller described some of these salts. P. Pascal gave 333×10^{-7} mass units for the mol. magnetic susceptibility of the PO_3-radicle of sodium salt.

Dimetaphosphates.—The acid itself has not been isolated, but A. Glatzel obtained an aq. soln. of **dimetaphosphoric acid,** $H_2P_2O_6$, by decomposing the silver salt in water by hydrogen sulphide. The soln. is unstable, and soon forms pyrophosphoric and orthophosphoric acids—particularly if heated. The soln. has acidic reactions, and when neutralized with alkali-lye gives a salt identical with that prepared in other ways. The dimetaphosphates were prepared by T. Fleitmann and W. Henneberg, R. Maddrell, and G. von Knorre, by heating an excess of phosphoric acid with the oxide, nitrate, or other salt of copper, manganese, zinc, or cobalt between 316° and 400°. The metals with a high at. wt.—*e.g.* barium, lead, cadmium, silver, and bismuth—usually give hexametaphosphates by this treatment; nickel and magnesium salts do not react in the same way. According to A. Glatzel, if, say, the zinc salt be treated with potassium sulphide, a soluble *potassium dimetaphosphate,* $K_2P_2O_6.H_2O$, is formed; with sodium sulphide, the corresponding *sodium dimetaphosphate,* $Na_2P_2O_6.2H_2O$, and with ammonium sulphide, *ammonium dimetaphosphate,* $(NH_4)_2P_2O_6$, is obtained. The other dimetaphosphates are obtained by double decompositions—*e.g.* chromium, ferric, nickel, cobalt, magnesium, barium, strontium, calcium, silver, lead, zinc, copper, etc. Of these salts, there are $MP_2O_6.4H_2O$, where M represents Cu, Zn, or Mn; and $M_2P_2O_6.2H_2O$, where M represents Na, Li, Pb, Ba, or Ca. The ammonium and silver salts are anhydrous; and the magnesium salt corresponds with $MgP_2O_6.4\frac{1}{2}H_2O$. Aluminium metaphosphate, $Al_2(P_2O_6)_3.nH_2O$, is also typical of the chromic and ferric salts, but whether these salts are really dimetaphosphates or not is an open question. The alkali salts are readily soluble in water, and crystallizable; the other salts are sparingly soluble in water. The less soluble salts are but little attacked by dil. hydrochloric or nitric acid, but boiling conc. sulphuric acid decomposes them completely, forming orthophosphates. The mol. wt. of the ammonium salt from the f.p. of aq. soln. is 118, the calculated value for $(NH_4)_2P_2O_6$ is 97. The ammonium salt is isomeric with hydrazine hypophosphate, $(N_2H_4)H_4P_2O_6$. Very conc. soln. of the ammonium salt crystallize as tetrahydrate, $(NH_4)_2P_2O_6.4H_2O$. According to T. Fleitmann, this salt passes into *ammonium monometaphosphate*, NH_4PO_3, when heated between 200° and 250°. *Copper dimetaphosphate*, $CuP_2O_6.4H_2O$, is imperfectly decomposed by hydrogen sulphide. There are cogent reasons for doubting the existence of the dimetaphosphates as chemical individuals. P. Pascal believed that the so-called dimetaphosphates are tetrametaphosphates; he gave 325×10^{-7} mass units for the mol. magnetic susceptibility of the PO_3 radicle of R. Maddrell's sodium salt. He found the change in diamagnetism with increasing complexity in the series of polymetaphosphates, is in the same direction and of the same order or magnitude as that caused by double bonds in organic compounds. This is in agreement with the view that R. Maddrell's salt is truly a dimetaphosphate. G. Tammann suggested they are really trimetaphosphates. An application of the electrolysis rule to soln. of the dimetaphosphates leads to the conclusion that the dimetaphosphates in aq. soln. at any rate, are salts of a tetrabasic acid, and hence F. Warschauer argued that T. Fleitmann's dimetaphosphates are really tetrametaphosphates. A. Holt and J. E. Myers failed to obtain the dimetaphosphates by the above process, and they conclude that the so-called alkali dimetaphosphates are "probably mixtures of the alkali salts and phosphoric acids, and not definite compounds." A. Glatzel reported about thirty complex double salts of the alleged dimetaphosphates of the general formula $M'_2M''P_2O_6.nH_2O$—*e.g.* $K_2Zn(P_2O_6)_2.6H_2O$; $K_2Cu(P_2O_6)_2.4H_2O$, etc.—from soln. containing eq. proportions of the two dimetaphosphates.

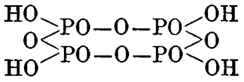
Trimetaphosphates.—T. Fleitmann and W. Henneberg prepared the sodium trimetaphosphate by heating sodium ammonium phosphate until the fused mass became crystalline. When extracted with water, insoluble monometaphosphate —R. Maddrell's salt—remains and the aq. soln. furnishes crystals of *sodium trimetaphosphate*, $Na_3P_3O_9.6H_2O$. Several other modes of preparation have been described, *e.g.* by G. Tammann, S. Tanatar, G. von Knorre, and L. Jawein and A. Thillot. A. Jamieson prepared it by heating sodium pyrophosphate with ammonium chloride: $Na_4P_2O_7+2NH_4Cl=2NaPO_3+2NH_3+2NaCl+H_2O$. According to G. von Knorre, the best method of preparation is to digest a mixture of disodium hydrogen phosphate, $Na_2HPO_4.12H_2O$, and ammonium nitrate, NH_4NO_3, in the proportion 1:3, for about 6 hrs. at 300°, and allow the clear aq. extract to crystallize. According to T. Fleitmann and W. Henneberg, sodium dimetaphosphate is obtained by heating sodium dihydrogen phosphate, although from determinations of the depression of the f.p., G. Tammann believed that the salt obtained by this process is a dimetaphosphate. P. Pascal gave 315×10^{-7} mass units for the mol. magnetic susceptibility of the PO_3-radicle of sodium trimetaphosphate. The sodium salt can be purified from pyro- and hexametaphosphates by first converting it into *lead trimetaphosphate*, $Pb_3P_3O_9.3H_2O$, by allowing a mixed soln. of the sodium salt and lead nitrate (not acetate) to stand for some days. The lead salt can be decomposed by digestion with sodium sulphate, and the sodium trimetaphosphate obtained in triclinic crystals of sp. gr. 2·476. The salt reacts like a neutral salt, with methyl-orange and phenolphthalein. The salt loses most of its water of crystallization over conc. sulphuric acid, or when heated on a water-bath; it is soluble in water, and very sparingly soluble in alcohol. According to A. Wiesler, the sodium salt is not converted into pyro- or ortho-phosphate when its aq. soln. is boiled, although S. Tanatar said that it is converted into pyrophosphate if allowed to stand for some time. *Silver trimetaphosphate*, $Ag_3P_3O_9.H_2O$, can be prepared in a similar manner to the lead salt, and most of the metal trimetaphosphates can be made by the action of the metal chloride or sulphate on the sodium salt. A soln. of free **trimetaphosphoric acid**, $H_3P_3O_9$, was prepared by A. Wiesler by the double decomposition of the silver salt or the lead salt. The acid is fairly stable in the cold, but is rapidly hydrolyzed to the normal ortho-acid on evaporation. C. G. Lindbom represented the constitution of the tribasic acid:



$$\begin{array}{l} HO \\ O \\ HO \end{array}\!\!\begin{array}{l} >PO-O \\ < \\ >PO-O \end{array}\!\!>PO-OH$$

The electrical conductivities of the sodium salt, by G. von Knorre, F. Warschauer, and G. Lammann, are in agreement with the tribasicity of the acid. S. Tanatar gave 15·15 Cals. for the heat of neutralization, $H_3P_3O_9+NaOH$. All the trimetaphosphates—even the silver and barium salts—are soluble in water. The potassium and ammonium salts are anhydrous; the manganese, cobalt, zinc, and copper salts crystallize with 9 mols. of water; the manganese salt also forms $Mn_3(P_3O_9)_2.11H_2O$; the ferrous salt, $Fe_3(P_3O_9)_2.12H_2O$; magnesium forms both $Mg_3(P_3O_9)_2.12H_2O$ and $Mg_3(P_3O_9)_2.15H_2O$. The trimetaphosphates readily form double salts—*e.g.* the double salt *calcium sodium trimetaphosphate*, $NaCaP_3O_9.3H_2O$, crystallizes from a mixed soln. of the sodium salt and calcium chloride; this and the other members of the series have the type formula $R''R'P_3O_9.nH_2O$, where R'' represents an atom of barium, strontium, or calcium, and R' an atom of sodium or potassium, or NH_4-radicle. Another series of double salts has the type formula $R''Na_4(P_3O_9)_2.nH_2O$, when R'' denotes an atom of cobalt, nickel, or cadmium. The salt $NiNaP_3O_9.4\frac{1}{2}H_2O$ has also been reported. The trimetaphosphates are perhaps better characterized than any of the salts of the other polymetaphosphoric acids; they all crystallize; and they are recognized by forming no precipitates with barium chloride or silver nitrate. P. Pascal agrees that the trimetaphosphates of A. Wiesler are correctly named.

Tetrametaphosphates.—T. Fleitmann prepared what he called tetrametaphosphates in colloidal masses by heating mixtures of the orthophosphates of the heavy metals with an excess of phosphoric acid at about 300°; according to A. Glatzel, salts or oxides may be used in place of the phosphate, and the calcination is made at a red-heat. In either case, the mass is extracted with water. When the product is digested with sodium or potassium sulphide, small crystals of the sodium or potassium salt are obtained. The electrical conductivity of the aq. soln. of the sodium salt corresponds with that required for a tetrabasic acid. The alkali salts prepared at the higher temp. form gum-like masses which do not pass through a filter-paper; while the alkali salts prepared at the lower temp. form crystals on evaporating the aq. soln., but not if precipitated by the addition of alcohol. The salts prepared at the higher temp. are thought to be hexametaphosphates. P. Pascal gave 298×10^{-7} mass units for the mol. magnetic susceptibility of the PO_3-radicle of sodium tetrametaphosphate. T. Fleitmann is reported to have made double salts by fusing mixtures of his copper and sodium dimetaphosphates —*e.g.* copper and sodium dimetaphosphates gave him $CuNa_2P_4O_{12}$. Tetrametaphosphates were also prepared by A. Glatzel, F. Warschauer, G. von Knorre, and G. Tammann. The first-named found the electrical conductivities of some of the salts fit in well with their tetrabasicity. G. Tammann said that the salts are hexa- or dodeca-metaphosphates; but P. Pascal considered that the tetrametaphosphates of F. Warschauer, and G. Tammann are correctly named. The aq. soln. of tetrametaphosphoric acid, $H_4P_4O_{12}$, was made by A. Glatzel, and F. Warschauer by treating the insoluble metal salts—*e.g.* those of silver or lead—suspended in water with hydrogen sulphide. The aq. soln. can be kept for a short time, but it rapidly passes into the pyro-acid, and finally into the ortho-acid. The products obtained by neutralizing the acid with alkali-lye are identical with those obtained in other ways. A. Glatzel represented the constitution:



Pentametaphosphates.—G. Tammann reported that he had made *ammonium pentametaphosphate*, $(NH_4)_5P_5O_{15}$, by heating ammonium dimetaphosphate at 200°–250°, and treating the resulting mass with water. The same salt is made by dissolving ammonium decametaphosphate in hot water; alcohol precipitates the salt from this soln. in white amorphous masses which have not been obtained in the crystalline state, but if the soln. be evaporated on a clock glass a stellate film is formed. G. Tammann measured the electrical conductivities of the soln. When this salt is treated with potassium bromide, **ammonium potassium pentametaphosphate**, $K_4(NH_4)P_5O_{15}.6H_2O$, separates from the soln.; similarly, sodium or lithium chloride gives an analogous **ammonium sodium pentametaphosphate**, $Na_4(NH_4)P_5O_{15}$, or **ammonium lithium pentametaphosphate**, $Li_4(NH_4)P_5O_{15}$. The potassium salt furnishes a crystalline mass, the others form gum-like masses on evaporating the aq. soln. There are several other differences between the potassium and ammonium salts—$K_4(NH_4)P_5O_{15}$ and $(NH_4)_4(NH_4)P_5O_{15}$—and the sodium and lithium salts—$Na_4(NH_4)P_5O_{15}$ and $Li_4(NH_4)P_5O_{15}$. For instance, the behaviour of the two series of salts towards reagents is not quite the same; and the electrical conductivities of the lithium and sodium salts agree with the assumption that each salt furnishes five cations, while the other salts furnish one cation, and thus behave like salts of a monobasic acid. It is therefore inferred that $[M_4P_5O_{15}]'$ behaves as a monobasic complex ion, an inference which is confirmed by the subtitutions just indicated. By treating the ammonium salt with silver nitrate, a pulverulent salt with the empirical composition $AgPO_3.\frac{1}{2}H_2O$ is obtained. When this is treated with the ammonium salt, it furnishes a crystalline product, $Ag_4(NH_4)P_5O_{15}.2H_2O$. Solutions of the sodium and lithium salts (1) give no precipitates with mercuric or cadmium chlorides, or with cupric sulphate—although the ammonium salt does give a gum-like mass; (2) with barium or ferric chloride and lead nitrate, precipitates are formed which are insoluble in an excess of reagent, (3) strontium chloride, or bismuth or silver nitrate gives a flocculent precipitate soluble in an excess of reagent; and (4) calcium chloride, or nickel, cobalt, manganese, zinc, ferrous, or aluminium sulphate gives a gum-like separation or a flocculent precipitate. The solubilities of these precipitates in an excess of their components indicates the formation of complex salts. The free acid has not been made.

Hexametaphosphates.—H. Lüdert prepared *sodium hexametaphosphate* by gradually heating disodium hydrogen pyrophosphate to a red-heat, and rapidly cooling the fused mass; it is also made by fusing monosodium hydro-orthophosphate, or microcosmic salt, so that T. Graham's salt is considered to be more or less impure sodium hexametaphosphate. T. Fleitmann considered that T. Graham's salt is a hexametaphosphate, since five of the sodium atoms can be replaced by ammonium, forming a substance with the empirical composition $(NH_4)_5NaP_6O_{18}$, but he did not prove that the fused salt is not a mixture of sodium monometaphosphate or of some other metaphosphate with a different polymeric form. G. Rose showed that soln. of T. Graham's salt furnish precipitates partly flocculent and partly gelatinous, when mixed with many salts of the metals or alkaline earths, *e.g.* by pouring the freshly prepared soln. into an excess of silver nitrate, two distinct layers are formed: (*a*) a crystalline salt, and (*b*) a gelatinous or resinous layer which is insoluble in water, and which appears to have the composition $Ag_5NaP_6O_{18}$. The crystalline salt is probably *silver hexametaphosphate*, $Ag_6P_6O_{18}$, which when treated with sodium chloride furnishes *sodium hexametaphosphate*, $Na_6P_6O_{18}$; and when this is digested with ammonium chloride, a salt, $(NH_4)_5NaP_6O_{18}$, is formed. Hence, G. Tammann obtained sodium hexametaphosphate from Graham's salt by first producing the crystalline silver salt, and then converting it into the sodium salt by treatment with sodium chloride. T. Fleitmann said that the acid itself can be made by calcining orthophosphorous acid. H. Lüdert obtained it by treating with hydrogen sulphide the lead or silver salt suspended in water. The aq. soln. is very unstable, and is readily hydrated, and, as A. Wiesler said, gives no information as to the basicity of the acid. G. Tammann believed that the sodium salt is really a mixture of $Na_6(PO_3)_6$ and two other hexametaphosphates, $Na_5[Na(PO_3)_6]$, and $Na_4[Na_2(PO_3)_6]$. This is inferred from the electrical conductivities of $K_2Na_4(PO_3)_6$ and $Na_2Na_4(PO_3)_6$, which show that two of the atoms of the alkali metal per mol are ionized. The salts may be *bis*-hexametaphosphates or *tris*hexametaphosphates, but probably are hexametaphosphates. The so-called a-monometaphosphoric acid may be identical with hexametaphosphoric acid. A. Wiesler prepared some of these salts. P. Pascal gave 289×10^{-7} mass units for the mol. magnetic susceptibility of the PO_3-radicle in T. Graham's sodium hexametaphosphate.

P. Pascal prepared *ethyl hexametaphosphate*, $(C_2H_5PO_3)_6$, by treating phosphoric oxide with absolute alcohol for some hours at the boiling temp., or some months at room temp. The viscous liquid is insoluble in ether, but soluble in chloroform. When fractionally precipitated by ether from its soln. in chloroform, about 12 per cent. of a polymer insoluble in chloroform is obtained. Ethyl hexametaphosphate has the mol. wt. required for $(C_2H_5PO_3)_6$, when its effect on the f.p. of naphthalene is determined. It gives sodium monometaphosphate when treated with sodium ethoxide. The alkali hexametaphosphates are best prepared by fusing the trimetaphosphate in small portions at a time in a platinum crucible at about 700°, and rapidly cooling the fused mass by plunging the bottom of the crucible in cold water. The transition temp. to the trimetaphosphate is 607°±2°. The change from the tri- to the hexa-metaphosphate is almost instantaneous, but the reverse change decreases rapidly with fall of temp., and is practically zero below 500°. The hexametaphosphates at a high temp. gradually become colloidal, as shown by the viscosity of the soln. There is a limit, 1·8 per cent. of colloid at 648° in 16 hrs.; and 1·2 per cent. in 6 hrs. at 835°. The hexametaphosphates are distinguished by forming complexes with iron and uranyl resembling the ferro- and ferricyanides —*e.g.* $M_4[Fe(PO_3)_6]$, $M_3[Fe(PO_3)_6]$, $M_4[UO_2(PO_3)_6]$. Consequently the hexametaphosphates decolorize ferric thiocyanate, and prevent the coloration of uranyl salts by potassium ferrocyanide. These reactions will detect the hexametaphosphates if one per cent. be present in a mixture. Graham's soluble salt behaves like a complex hexametaphosphate, $Na_2[Na_4(PO_3)_6]$. It is unstable in aq. soln., and in the presence of a lead salt precipitates lead hexametaphosphate from which the ordinary alkali hexametaphosphates can be prepared.

A number of still higher polymerized metaphosphates have been reported. According to G. Tammann, by melting a mol of a salt of a bivalent metal with a mol of sodium ammonium hydrophosphate, a clear fluid is obtained which crystallizes when the mass is cooled. The cubic or octahedral crystals have the composition of **octometaphosphates,** *e.g.* $Zn_3Na_2P_8O_{24}$—representing **octometaphosphoric acid,** $H_8P_8O_{24}$, magnesium, manganese, cobalt, nickel, or zinc sulphates may be used, but not barium, lead, or copper salts, for the latter give pyrophosphates. G. von Knorre had doubts about the chemical individuality of the octometaphosphates. By heating ammonium dimetaphosphate for two or three hours between 200° and 250°, G. Tammann prepared what he regarded as a **decametaphosphate,**

$(NH_4)_{10}P_{10}O_{30}$, which is partly changed by treatment with soln. of the metal salts—*e.g.* potassium hydroxide, or potassium chloride giving **ammonium ennea-potassium decametaphosphate,** $K_9(NH_4)P_{10}O_3.10H_2O$, as an insoluble crystalline powder. When the deca-salt is treated with hot water, two mol. eq. of pentametaphosphate are obtained. G. von Knorre had doubts about the chemical individuality of the decametaphosphates. When nickel or cobalt sulphate is melted with phosphoric acid containing some sodium salt, R. Maddrell reported that **sodium cobalt and sodium nickel tetradecametaphosphates,** $Ni_6Na_2P_{14}O_{42}$, or $Co_6Na_2P_{14}P_{42}$—representing **tetradecametaphosphoric acid,** $H_{14}P_{14}O_{42}$—are formed. G. Tammann also reported a *sodium magnesium tetradecametaphosphate*, $Na_2Mg_6(PO_3)_{14}$, but, added G. von Knorre, whether it is to be considered as a chemical individual or a mixture is open to question. P. Pascal gave for the three colloidal salts the mol. magnetic susceptibility 266×10^{-7}, 268×10^{-7}, and 268×10^{-7}, and for the non-colloidal salt 254×10^{-7}; and inferred that the colloidal salts are three forms of the octometaphosphate, and the non-colloidal salt is a decametaphosphate.

There is some doubt if some of the polymetaphosphates are really chemical individuals, and if some of the individual metaphosphates have been inserted in the right class. Decisive evidence is usually wanting, for, in spite of the many researches which have been made on the metaphosphates, their chemistry is by no means in a satisfactory condition. As F. Warschauer said in 1903, the metaphosphates form one of the most confused chapters of inorganic chemistry.

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§ 28. Polyphosphoric Acids

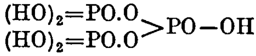
Pyrophosphoric acid can be considered as a member of a series of polyphosphoric acids. They can be derived from ordinary phosphoric acid by the abstraction of water, thus:

Pyrophosphoric acid, $H_4P_2O_7$	$2H_3PO_4$ less H_2O
Triphosphoric acid, $H_5P_3O_{10}$	$3H_3PO_4$ less $2H_2O$
Tetraphosphoric acid, $H_6F_4O_{13}$	$4H_3PO_4$ less $3H_2O$

The general formula is $mH_3PO_4-(m-1)H_2O$, or $H_nP_{n-2}O_4+(n-3)_3$. For example:

Orthophosphoric acid ($m=1$)	H_3PO_4
Di- or pyro-phosphoric acid ($m=2$)	$H_4P_2O_7$
Triphosphoric acid ($m=3$)	$H_5P_3O_{10}$
Tetraphosphoric acid ($m=4$)	$H_6P_4O_{13}$

Salts of some of these acids were made by T. Fleitmann and W. Henneberg,[1] P. Glühmann, F. Schwarz, and M. Stange, by heating metaphosphates with pyro- or ortho-phosphates. On cooling a fused mixture of anhydrous sodium pyrophosphate (100 parts) with sodium metaphosphate (50 parts) which has been kept at a bright red-heat for about half an hour, a crystalline mass of sodium triphosphate, $Na_5P_3O_{10}$, is obtained: $Na_4P_2O_7+NaPO_3=Na_5P_3O_{10}$. The conc. aq. soln. furnishes crystals corresponding with $Na_5P_3O_{10}.8H_2O$—a result not obtained by simply evaporating a soln. of the two salts in water, and which has been used against the argument that the alleged triphosphate is a double salt of sodium pyro- and meta-phosphates. The aq. soln. when boiled decomposes into a mixture of the two components. Various double salts have been prepared of the type $M''Na_3P_3O_{10}$, by treatment with cobalt, zinc, and other salts. Zinc and manganese salts of the type $M''_2NaP_3O_{10}$ have been made. M. Stange found that when titrated with 1 : 10 soln. of ferrous ammonium sulphate, lead nitrate, manganese sulphate, cadmium sulphate, or barium chloride rather more liquid is required to produce a precipitate with a soln. of triphosphate than with an eq. mixture of meta- and pyro-phosphates; rather less with a soln. of chrome-alum, and just the same with silver nitrate. F. Schwarz claims to have made the free acid —**triphosphoric acid,** $H_5P_3O_{10}$—by treating an aq. soln. of the copper salt with hydrogen sulphide. The aq. soln. of the acid is soon transformed into pyrophosphoric acid, $2H_5P_3O_{10}+H_2O \rightarrow 3H_4P_2O_7$, and albumen is not coagulated; if, however, the sodium salt is treated with a few drops of acetic acid, the albumen is coagulated. F. Schwarz represented the constitution



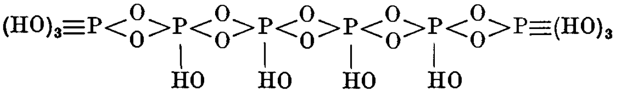
$$\left.\begin{matrix}(HO)_2=PO.O\\(HO)_2=PO.O\end{matrix}\right> PO-OH$$

in agreement with the phenyl triphosphate obtained by M. Riegel.

T. Fleitmann and W. Henneberg also prepared *sodium tetraphosphate*, $Na_6P_4O_{13}$ —representing **tetraphosphoric acid,** $H_6P_4O_{13}$—by melting together a mixture of eq. amounts of sodium hexametaphosphate, $Na_6P_6O_{18}$, and sodium pyrophosphate: $Na_6P_6O_{18}+3Na_4P_2O_7=3Na_6P_4O_{13}$; or with sodium orthophosphate: $Na_6P_6O_{18}+2Na_3PO_4=2Na_6P_4O_{13}$. Sodium tetraphosphate can be crystallized from its soln. in hot water, although it is slowly transformed into the orthophosphate in warm aq. soln. An acid salt has not been made, but silver and magnesium salts of a similar composition have been made by double decomposition of the sodium salt with salts of the respective elements. If sodium salts were those of a hexametaphosphate, they should give no precipitate with magnesium salts, and with silver salts a precipitate soluble in an excess of the sodium salt. C. F. Gerhardt thought the salt crystallizing with 18 mols. of water of crystallization to be an acid salt of pyrophosphoric acid, but K. Kraut and H. Uelsmann found that this is not likely to be the case because all the water is lost in a desiccator over sulphuric acid. M. A. Rakusin and A. A. Arsenéeff found that after the violent reaction resulting from the addition of phosphoric oxide to water and formation of orthophosphoric acid has subsided, further quantities are gradually added until the amount reaches about 520 per cent. of the water present. After keeping for five days, crystals of tetraphosphoric acid, $H_6P_4O_{13}$, separate from the syrupy liquid. This acid has previously only been prepared in the form of its salts. The acid melts at 34°, and has a sp. gr. of 1·8886 at 15°.

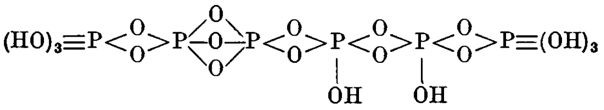
T. Fleitmann and W. Henneberg also prepared **sodium decaphosphate,** $Na_{12}P_{10}O_{31}$,—representing **decaphosphoric acid,** $H_{12}P_{10}O_{31}$—by fusing together eq. quantities of sodium hexametaphosphate and sodium pyrophosphate: $4Na_6P_6O_{18}+3Na_4P_2O_7=3Na_{12}P_{10}O_{31}$.

A. V. Kroll[2] reported a series of salts which he called *ultra-phosphates*, but the following is not his view of their nature. Assuming the ultra-phosphates are chemical individuals, they can be derived from the **orthohexaphosphoric acid,** $H_{20}P_6O_{25}$, or $(HO)_4P.O.P(OH)_3.O.P(OH)_3.O.P(OH)_3.O.P(OH)_3.O.P(OH)_4$, by the loss of five mols. of water so as to form **penterohexaphosphoric acid,** $H_{10}P_6O_{20}$, represented by **calcium penterohexaphosphate,** $5CaO.P_2O_5$, or $C_5P_6O_{20}$—for the nomenclature, *vide* the silicic acids, **6.** 40, 22.

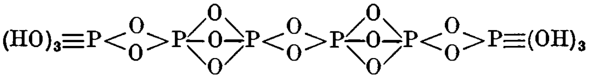


$$(HO)_3\equiv P{<}{}^{O}_{O}{>}\underset{\displaystyle HO}{\underset{|}{P}}{<}{}^{O}_{O}{>}\underset{\displaystyle HO}{\underset{|}{P}}{<}{}^{O}_{O}{>}\underset{\displaystyle HO}{\underset{|}{P}}{<}{}^{O}_{O}{>}\underset{\displaystyle HO}{\underset{|}{P}}{<}{}^{O}_{O}{>}P\equiv(HO)_3$$

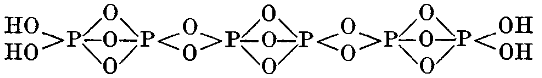
is obtained as a fused mass by passing the vapour of phosphoric oxide over heated lime; lead oxide furnishes the corresponding lead salt; and magnesium and nickel salts have been made. The tetrabasic phosphate, Thomas' slag, **calcium hexerohexaphosphate,** $4CaO.3P_2O_5$, and the lead salt, $4PbO.3P_2O_5$, representing the **hexerohexaphosphoric acid,** $H_8P_6O_{19}$:



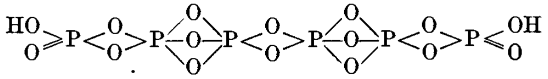
The next member of the series would be **hepterohexaphosphoric acid,** $H_6P_6O_{18}$:



which is isomeric with hexametaphosphoric acid, and represented by the hydrate, $2Na_2O.3P_2O_5.H_2O$, or $Na_4H_2P_6O_{18}$. When the vapour of phosphorus pentoxide acts on lime at 250°, the resulting **calcium octerohexaphosphate,** $2CaO.3P_2O_5$, or $Ca_2P_6O_{17}$, representing **octerohexaphosphoric acid,** $H_4P_6O_{17}$:



Corresponding lead, lithium, and sodium salts have been prepared. The last member of this series of salts is represented by the lithium, sodium, silver, and lead salts, $R_2O.3P_2O_5$, corresponding with **ennerohexaphosphoric acid,** $H_2P_6O_{16}$;



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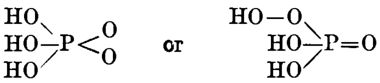
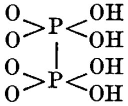
[2] A. V. Kroll, *Ueber Ultraphosphate*, Leipzig, 1912; *Zeit. anorg. Chem.*, **76.** 387, 1912; **77.** 1, 1912; **78.** 95, 1912; *Journ. Iron Steel Inst.*, **84.** ii, 126, 1911; *Stahl Eisen*, **28.** 675, 1908; **31.** 2020, 1911.

§ 29. Perphosphoric Acids

Orthophosphoric acid does not react with hydrogen dioxide, and there are no signs of the formation of a perphosphoric acid, analogous with persulphuric acid, when soln. of phosphoric acid are electrolyzed. J. Schmidlin and P. Massini,[1] and J. d'Ans and W. Friederich found the case to be different, however, if phosphorus pentoxide be treated with 30 per cent. hydrogen dioxide at low temp., for when the mixture is diluted with ice-cold water, a soln. is obtained which has oxidizing properties analogous to those possessed by permonosulphuric acid. If a dil. soln. of phosphoric acid containing hydrogen dioxide be electrolyzed, permonophosphoric acid is also obtained. Analyses correspond with **permonophosphoric acid,** H_3PO_5, or $PO(OH)_2O.OH$. A similar compound is obtained with meta- and pyro phosphoric acids; in the latter case, also, a small quantity of **perdiphosphoric acid,** $H_4P_2O_8$, is formed, particularly if the pyrophosphoric acid be in excess. The compositions of the permonophosphoric and permonosulphuric acids are different since the sulphur in the one case is sexivalent, and the phosphorus in the other case is quinquevalent:



Permonophosphoric acid.



Perdiphosphoric acid.

The proportion of $H_4P_2O_8$ which is formed is greater the greater the excess of pyrophosphoric acid over the hydrogen dioxide; for example, with 3 c.c. of dioxide to 25 c.c. of syrupy pyrophosphoric acid, the acid formed corresponded with 20 per cent. active oxygen, and with 40 per cent. active oxygen when the respective proportions were 1 : 42. Permonophosphoric acid oxidizes manganous salts to permanganates in the cold, a reaction not shown by Caro's acid, and it liberates iodine from potassium iodide. No salts—permonophosphates—have been obtained, although soln. (not acidic soln.) give precipitates with silver, iron, nickel, manganese, and salts of the heavy metals, and these rapidly change to orthophosphates with the evolution of ozonized oxygen. Conc. soln. have a smell resembling that of bleaching powder; they do not keep so well as more dil. soln. Neutral and alkaline soln. are less stable than acidic soln. G. I. Petrenko reported **sodium perphosphate,** $(NaO)PO(O_2Na)_2.6\frac{1}{2}H_2O$, as a result of treating a soln. of sodium phosphate with hydrogen dioxide; it is thought to be sodium phosphate with hydrogen dioxide of crystallization, $Na_3PO_4.2H_2O_2.4\frac{1}{2}H_2O$; and E. Pinerua-Alvarez prepared a compound $NaPO_4$ by the action of a soln. of sodium dioxide in aq. alcohol on sodium phosphate. A. R. y Miro obtained perphosphates by the electrolytic oxidation of phosphates with an electrolyte containing fluorides; the anodic oxidation of phosphates was also studied by F. Fichter and J. Müller; and the oxidation of phosphoric acid (*q.v.*) by fluorine, by F. Fichter and W. Bladergroen. S. Aschkenasy made the **alkaline earth perphosphates** by dissolving the peroxides in an excess of phosphoric acid; on evaporating the soln. under diminished press., the perphosphate is produced. If an alkali sulphate be added to the liquid before evaporation, the filtrate furnishes an **alkali perphosphate.** F. H. Fuhrmann summarized the patent literature on the subject.

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§ 30. Phosphorus Fluorides

Phosphorus unites directly with the halogens in at least two different proportions—three, the fluorides, chlorides, and bromides, are of the types, PX_3 and PX_5, while the iodides are PI_3 and P_2I_4—there is also a chloride corresponding with this latter compound. The pentahalides are obtained by treating the trihalides with more halogen; the reaction is reversible, and the vapour of the pentahalide is more or less dissociated: $PX_5=PX_3+X_2$. The affinity of phosphorus for the halogens decreases with increasing at. wt.—*e.g.* the pentafluoride is the most stable higher compound, and the pentaiodide, if it has been prepared at all, is a very unstable product; the heats of formation of the trihalides decrease in the same direction:

	PF_3	PCl_3	PBr_3	PI_3
Heats of formation	108	76	44·8	10·5 Cals.
Boiling points .	−95°	76°	175°	decomposes
Melting points .	−160°	−111·8°	−41·5°	60°

The corresponding chemical properties, and also the physical properties, usually change more or less regularly in passing from one end of the series to the other. A number of mixed halides are also known, for instance, PF_5(gas), PF_3Cl_2(gas), PF_3Br_2(liquid), PF_3I_2(solid), etc.; there are also some oxy-halides, *e.g.* $POCl_3$, $POBr_3$, $POClBr_2$, etc., as well as $P_2O_3Cl_4$, PO_2Cl, etc.

H. Davy,[1] and J. B. A. Dumas prepared a fuming liquid resembling phosphorous chloride, PCl_3, by heating phosphorus with lead or mercuric fluoride. According to J. L. Gay Lussac and L. J. Thénard, this reaction only occurs in the presence of silica, and L. Pfaundler noticed that when the materials are heated in a glass tube, most of the phosphorus distils unchanged; only where the materials are in contact with the glass does etching and decomposition occur; and the product of the reaction is a vapour which does not condense at −20°. R. W. E. MacIvor also said that phosphorus fluoride is a gas at ordinary temp. and press. It was afterwards shown that phosphorus fluoride must be a gas at ordinary temp. and therefore the liquid obtained by H. Davy could not have been the fluoride. The nature of the fluorides of phosphorus was not clear until the advent of H. Moissan's investigations on fluorine, mainly recorded in his monograph *Le fluor et ses composés* (Paris, 1900). It is there shown that yellow or red phosphorus burns vigorously in fluorine gas; and when fluorine is led through a fluorspar tube containing a piece of dry phosphorus, the pentafluoride is formed, and if the phosphorus be in excess, some trifluoride as well as pentafluoride appears among the products of the reaction.

In 1884, H. Moissan[2] prepared **phosphorus trifluoride,** or **phosphorous fluoride,** PF_3, by heating a mixture of lead fluoride and copper phosphide to dull redness in a brass tube closed at one end, and fitted by means of a cork at the other end with a lead exit tube. This end of the brass tube is kept cool by a water-jacket. The gas was first passed through a wash-bottle containing a few c.c. of water to remove traces of hydrogen fluoride or phosphorus pentafluoride; and then dried by passage through a vessel containing sulphuric acid. The dry gas can be collected over mercury. H. Moissan also made the gas by the action of silver, zinc, or arsenious fluoride on phosphorus trichloride; and by the action of zinc fluoride on phosphorous bromide. A. Guntz made it by the action of lead fluoride on phosphorus trichloride; C. Poulenc, and H. Moissan, by the action of hydrogen at 250°, or of the metals—mercury, aluminium, tin, lead, iron, or nickel—at 180°, or of phosphorus at 120° on phosphorus dichlorotrifluoride; H. Moissan, by passing induction sparks through phosphorus pentafluoride: $PF_5=PF_3+F_2$; and A. Simon, by the electrolysis of soln. of the oxides of iron or manganese in molten calcium fluoride in the presence of carbon; the resulting carbon tetrafluoride acting on phosphorus or the metal phosphides yields phosphorus trifluoride: $2Mn_3P_2+3Mn+3CF_4=3Mn_3C+4PF_3$.

According to H. Moissan, phosphorus trifluoride is a colourless gas which does not fume in air, and which can be condensed to a colourless, mobile liquid which does not attack glass. The vapour density is 3·022, and the value calculated for PF_3 is 3·045. This formula is also in accord with H. Moissan's analysis. The mol. vol. of the gas at 0° and 760 mm. is 153·24 c.c. Phosphorus trifluoride does not change when heated to 500° for half an hour in an iron vessel, but in a glass vessel, or in the presence of silica, it decomposes very quickly: $4PF_3+3SiO_2=3SiF_4+3O_2+4P$. The amount of oxygen formed is not sufficient to convert all the phosphorus into the pentoxide. The b.p. of the liquid is −95°; and it can be frozen to a snow-white solid with a m.p. −160°. M. Berthelot obtained for the heat of formation of the gas from its elements 106·2 to 109·7 Cals. When phosphorus trifluoride is sparked in a glass tube with platinum electrodes, H. Moissan found that the spectrum shows many lines due to fluorine, to phosphorus, and to platinum. The phosphorus lines are very intense, whilst those of fluorine are feebler. The dry gas is decomposed by the electric discharge: $5PF_3=3PF_5+2P$. If a trace of moisture be present, the phosphorus deposits on the walls of the vessel, the vol. decreases, and the residue contains some silicon tetrafluoride formed by the action of hydrogen fluoride on the glass containing-vessel.

According to H. Moissan, when a mixture of phosphorus trifluoride and **hydrogen** is heated, hydrogen fluoride and phosphine are produced: $PF_3+3H_2=PH_3+3HF$. The hydrogen fluoride immediately attacks the glass, forming silicon tetrafluoride. The trifluoride does not burn in **air,** but if mixed with **oxygen,** the gas explodes, forming phosphoryl fluoride: $2PF_3+O_2=2POF_3$; and oxygen in excess of this proportion remains as an inert gas. A mixture of the gas with half its vol. of oxygen explodes vigorously when sparked, but it is not ignited by the flame of coal gas. The temp. is here not sufficiently high, for if the mouth of the gas-jar containing the mixture approaches the oxyhydrogen flame, the gas is ignited and the flame travels to the bottom of the jar. Phosphorus trifluoride reacts slowly with **water** at 20°, forming phosphorous and hydrofluoric acids; the reaction is not quite analogous to the reaction between water and phosphorus trichloride—*vide infra.* With boiling water or steam, the reaction proceeds more quickly, but not instantaneously. The trifluoride is not absorbed by dry **potassium hydroxide,** but with an aq. soln. of potassium or **sodium hydroxide,** the alkali fluoride and phosphite are produced, and not, as M. Berthelot supposed, potassium fluophosphate. The gas is slowly absorbed by aq. soln. of **potassium carbonate,** or of **barium hydroxide.** Absolute **alcohol** absorbs the gas with the development of much heat, forming an ethereal liquid which does not give off a gas when boiled. A yellow flame appears when the trifluoride comes in contact with **fluorine,** and the pentafluoride is formed; and H. Moissan, and C. Poulenc found that in contact with **chlorine,** the dichlorotrifluoride is formed; with **bromine,** the dibromotrifluoride; and with **iodine,** the dichlorotrifluoride. H. Moissan found that when **hydrogen chloride** is heated with the trifluoride, phosphine, and phosphorous chloride are formed. When the trifluoride is heated with **sulphur** vapour to 440°, no change can be detected. The dry trifluoride reacts with dry **ammonia,** forming a white flocculent mass which is immediately decomposed by water. No reaction occurs when the gas is heated with **phosphorus**; and **arsenic** can be sublimed in the gas without forming arsenic fluoride. This shows that phosphorus trifluoride is more stable than arsenic trifluoride. When phosphorus trifluoride is heated in contact with **boron,** in a glass vessel, the reaction furnishes phosphorus, boron trifluoride, and a little silicon tetrafluoride; with **silicon,** at a full red-heat, phosphorus and silicon tetrafluoride are formed: $4PF_3+3Si=3SiF_4+4P$, a reaction utilized for analyzing the gas. A. Simon represented the reaction with heated **silica**: $4PF_3+3SiO_2=3SiF_4+3O_2+4P$; and, as indicated above, the silica of **glass** is attacked in virtue of a similar reaction. If a piece of **sodium** be heated in phosphorus trifluoride confined over mercury, the metal melts, and the vol. of the gas then gradually decreases, until suddenly the metal becomes incandescent, and the whole of the gas is rapidly absorbed; with heated **copper,** the metal acquires a film of phosphide, the vol. of the gas decreases, and silicon tetrafluoride appears. A. Granger said that at a red-heat, copper dipentitaphosphide is formed. H. Moissan found that with **mercury** vapour no visible action occurs at 350°, aluminium has but a slight action even at the softening temp. of glass. This, said H. Moissan, seems remarkable because of the ease with which aluminium fluoride is prepared—the probable explanation is that a protective film of fluoride is formed on the surface of the metal. A. Granger found that the phosphorus trifluoride reacts with **iron, cobalt,** and **nickel** at a high temp., forming phosphides—the products are contaminated with fluorides, and decomposition products of the glass containing-vessel. When the gas is passed quickly over spongy **platinum** at a red-heat, phosphorus pentafluoride is formed; but if the gas is passed slowly, it is completely absorbed by the red-hot spongy platinum. H. Moissan found that soln. of **chromic acid,** or of **potassium permanganate,** rapidly decompose phosphorus trifluoride, forming phosphoric acid, etc.

In 1887, T. E. Thorpe[3] discovered **phosphorus pentafluoride,** or **phosphoric fluoride,** PF_5. He found that when arsenic fluoride is added drop by drop to phosphorus pentachloride contained in a small flask, a vigorous reaction occurs, a colourless fuming gas is given off, and arsenic chloride remains. The reaction is symbolized: $5AsF_3+3PCl_5=3PF_5+5AsCl_3$. The gas is contaminated with the vapours of arsenious fluoride and chloride. A. Guntz made the pentafluoride by the action of phosphorus pentachloride on lead fluoride; and H. Moissan made the same gas by sparking phosphorus trifluoride: $5PF_3=2P+3PF_5$; and by leading a rapid stream of phosphorus trifluoride through a heated tube of platinum sponge—yield 12–13 per cent. A fairly pure product was also obtained by the spontaneous decomposition of phosphorus trifluodibromide at 15°; in symbols: $5PF_3Br_2=3PF_5+2PBr_5$. The pentafluoride is a gas, and the pentabromide is a solid. The gas is contaminated with bromine, which can be removed by allowing it to stand in a dry flask in contact with mercury. C. Poulenc made the gas by heating phosphorus trifluodichloride to 200°–250°, or by passing an electric discharge through that gas. H. J. Lucas and F. J. Ewing obtained the pentafluoride by heating in an iron tube a mixture of 25 grms. of phosphorus pentoxide, and 55 grms. of dry calcium (not potassium) fluoride: $5CaF_2+6P_2O_5=2PF_5+5Ca(PO_3)_2$.

According to T. E. Thorpe, and H. Moissan, phosphorus pentafluoride is a colourless fuming gas with a powerful smell; it rapidly attacks the respiratory organs. It is heavy enough to be poured like carbon dioxide from one vessel to another. The gas is incombustible and a non-supporter of combustion. It can be kept over mercury for some time, but its volume gradually diminishes. According to T. E. Thorpe, the vapour density is 126 (H=2), and its formula is therefore PF_5, where phosphorus is undoubtedly quinquevalent. T. E. Thorpe found that at 7° and under a press. of 12 atm., the gas exhibits no marked deviation from the standard gas law. H. Moissan said the gas liquefies under a press. of 46 atm. at 15°, and if the press. is partially released the gas solidifies, but rapidly returns to the liquid condition. Notwithstanding the care taken in drying the gas, a certain quantity always remains unliquefied, but if the pressure is raised from 46 atm. to 125 atm. the meniscus disappears. The whole of the space above the mercury has the same index of refraction. This is the critical point, and hence it is possible by means of phosphorus pentafluoride to exhibit the liquefaction, solidification, and critical point of a gas at the ordinary temp. The gas can be condensed to a liquid boiling at —75°, and frozen to a solid melting at 83°. H. Moissan examined the spectrum of the gas in a discharge tube with platinum electrodes. There are fewer spectral lines with the pentafluoride than with the trifluoride, and this is taken as evidence of the greater stability of the former gas. If thoroughly dried, phosphorus pentafluoride is not changed by feeble electric sparks, but is decomposed ($PF_5=PF_3+F_2$) by intense electric sparks, and both the glass and the surface of the mercury are attacked by the fluorine; similarly, T. E. Thorpe, and H. Moissan found that it is not affected by feeble electric sparks if mixed with *hydrogen* or *oxygen*. T. E. Thorpe said that the pentafluoride is decomposed by *water*, forming hydrofluoric and phosphoric acids; if the gas is pure, added H. Moissan, the absorption of the gas by water is complete. If a trace of moisture is present when the gas is confined in a glass vessel, silicon tetrafluoride and phosphoryl fluoride are formed, and some of the alkali in the glass forms a fluophosphate, or phosphate. The pentafluoride is not attacked by *fluorine*, hot or cold; nor does *iodine* attack the gas at temp. up to 500°. The vapour of *sulphur* at 440° has no perceptible action. T. E. Thorpe said that the gas forms a yellow **phosphorus hemipentamminofluoride,** $PF_5.5NH_3$, when brought in contact with dry *ammonia;* this compound dissolves in water, and the soln. etches glass. E. Tassel found that phosphorus pentafluoride reacts with *nitrogen peroxide* at —10°, forming a mass of white crystals of **phosphorus dinitroxylpentafluoride,** $PF_5.N_2O_4$. The crystals of this compound fume in air; and dissociate at ordinary temp., and particularly when heated $PF_5.N_2O_4 \rightleftharpoons PF_5 + N_2O_4$; water decomposes it into nitric oxide, and nitric, phosphoric, and hydrofluoric acids; and conc. sulphuric acid liberates the pentafluoride, forming a substance which is decomposed by water, forming nitrosyl sulphate. Returning to phosphorus pentafluoride, H. J. Lucas and F. J. Ewing did not obtain isoamyl fluoride by the action of phosphorus pentafluoride on boiling dry isoamyl alcohol for $1\frac{1}{2}$ hrs. H. Moissan found that the pentafluoride attacks *platinum* sponge at a red-heat, liberating fluoride, and forming a platinum fluophosphide.

H. Schulze[4] obtained **phosphorus oxytrifluoride,** or **phosphoryl fluoride,** POF_3, by the action of phosphorus pentoxide on a fluoride; T. E. Thorpe and J. F. Hambly, by heating a mixture of phosphorus pentoxide and cryolite in a brass tube, and collecting the gas over mercury as soon as a sample is all absorbed by water; and H. Moissan, by the action of phosphorus pentoxide on anhydrous hydrogen fluoride; by sparking a mixture of 2 vols. of the phosphorus trifluoride with one vol. of oxygen, or by passing the same mixture over platinum sponge. H. Moissan also made phosphoryl fluoride by the action of phosphoryl chloride on silver or zinc fluoride contained in a brass tube fitted with a lead delivery tube: $POCl_3+3AgF=3AgCl+POF_3$. The evolution of gas begins at ordinary temp., and it is passed through a tube containing lead fluoride to remove traces of phosphoryl chloride. A. Guntz used lead fluoride in place of silver or zinc fluoride; and C. Poulenc, and H. Moissan obtained the gas by the action of water on phosphorus dichlorotrifluoride: $PF_3Cl_2+H_2O=POF_3+2HCl$. At ordinary temp., phosphoryl fluoride is a gas which fumes in air; and if thoroughly dried, does not attack glass. According to H. Moissan, and T. E. Thorpe and J. F. Hambly, its analysis corresponds with the formula POF_3, and this simple formula is also in agreement with their determinations of the vap. density. H. Moissan obtained 3·68 to 3·71 when the calculated value is 3·69 (air unity); and T. E. Thorpe and J. F. Hambly, 52·3, when the calculated value is 52·0 (H unity). H. Moissan found that the gas can be condensed to a liquid boiling at —40°; and solidified to a snow-white crystalline mass melting at —68°. When heated in a glass vessel, phosphoryl fluoride does not decompose so easily as phosphorus trifluoride, and it forms silicon tetrafluoride and an alkali phosphate. The gas is not attacked by fluorine in the cold, and water absorbs the gas with the development of heat, forming phosphoric and hydrofluoric acids; alcohol acts in an analogous way; and the gas is likewise quickly absorbed by a soln. of chromic oxide, or alkali-lye. W. Lange found that **difluo-dioxyphosphoric acid,** $POF_2.OH$, is a product of the hydrolysis of phosphoryl fluoride; and the ions of this acid are present in a soln. of phosphoric oxide in hydrofluoric acid. He also prepared **ammonium difluodioxyphosphate,** $(NH_4)PO_2F_2$.

H. Moissan[5] said that when phosphorus trifluoride is treated with water, the phosphorus is not converted into a phosphite or a phosphate, but into some compound which cannot be converted into a phosphate even by boiling with dil. nitric acid. M. Berthelot said that the heat developed by the action of water is 107·7 cals. per mol, a lower value than is the case with the corresponding chloride or bromide. This is because **hydrofluophosphorous acid,** HPF_4, is formed analogous to hydrofluoboric or hydrofluosilicic acids: $2PF_3+3H_2O=H_3PO_3+2HF+HPF_4$. The acid appears to form an **alkali fluophosphite** when treated with dil. alkali-lye. The hydrofluophosphorous acid is stable enough to resist splitting into a phosphite and fluoride by boiling with an excess of alkali-lye. If the liquid obtained by the action of the trifluoride on water be titrated with standard alkali soln., using methyl-orange as indicator, it appears as if the reaction is $5PF_3+12H_2O=11HF+4H_3PO_3+HPF_4$. The nature of the decomposition probably varies according to the conditions. The facts are also explained by assuming that a **phosphoryl monofluoride**, POF, is formed. So that the nature of the reaction has not yet been established.

Some fluophosphates obtained by H. Briegleb, and others have been discussed, 2. 20, 39. Free **monofluo-orthophosphoric acid,** $P(OH)_4F$, has not been obtained, but R. F. Weinland and J. Alfa[6] reported **potassium monofluotrihydrorthophosphate,** $P(OH)_3(OK)F$, to be formed by evaporating equimolar proportions of potassium hydrophosphate and potassium hydroxide to dryness, dissolving it in 40 per cent. hydrofluoric acid, and cooling the concentrated soln. by a freezing mixture. Colourless, lustrous plates belonging to the monoclinic system are formed; the axial ratios are $a:b:c=0{\cdot}8501:1:0{\cdot}6268$. The crystals are stable in dry air, but in moist air they lose hydrogen fluoride. The salt cannot be crystallized from water or hydrofluoric acid, and it loses hydrogen fluoride when heated. When the temp. is high enough the salt melts to a glass. It gives off hydrogen fluoride when treated with sulphuric acid. The corresponding **rubidium monofluotrihydrorthophosphate,** P(OH)(ORb)F, and **cæsium monofluotrihydrorthophosphate,** P(OH)OCs)F, have been reported.

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§ 31. Phosphorus Dichloride and Trichloride

According to A. Gautier,[1] **phosphorus dichloride,** PCl_2, or perhaps P_2Cl_4, cannot be obtained by the action of the corresponding diiodide on silver chloride; but, according to A. Besson and A. Fournier, on submitting a mixture of phosphorus trichloride and hydrogen to the action of an electric discharge, a colourless liquid, holding in suspension a yellow solid, is produced. After filtration and purification by distillation under diminished pressure in an inert atmosphere, the liquid has a composition corresponding with that of phosphorus dichloride. It is a colourless, oily, and strongly fuming liquid. The fuming is not only caused by the action of moisture, but also by oxidation, and under certain conditions the liquid takes fire spontaneously. It boils, with decomposition, at about 180° at 760 mm. press., and at 95°–96° and 20 mm. press. without decomposition; it melts at —28°. It is decomposed by water with the formation of phosphorous acid and a yellow solid of indefinite composition. It decomposes slowly at the ordinary temperature, and more quickly when heated, to form phosphorus trichloride and a yellow to red solid of indefinite composition, which is possibly a mixture of amorphous phosphorus with other chlorides.

J. L. Gay Lussac and L. J. Thénard[2] about 1808, and H. Davy about 1810, prepared liquid **phosphorus trichloride,** or **phosphorous chloride,** PCl_3, by the action of chlorine on phosphorus. If the phosphorus be in excess, the liquid trichloride is formed, and if the chlorine be in excess, the pentachloride is produced as indicated in connection with the *la reaction très vive* between these two elements. H. Davy said:

> I introduced phosphorus into a receiver having a stopcock, which had been exhausted, and admitted oxymuriatic acid gas. As soon as the retort was full the phosphorus entered into combustion, throwing forth pale white flames. A white sublimate collected in the top of the retort, and a fluid as limpid as water trickled down the sides of the neck. The gas seemed to be entirely absorbed, for, when the stopcock was opened, a fresh quantity of oxymuriatic acid gas, nearly as much as could have filled the retort, entered. The same phenomenon of inflammation again took place, with similar results. Oxymuriatic acid gas was admitted until the whole of the phosphorus was consumed.

The liquid proved to be phosphorus trichloride, the solid, phosphorus pentachloride. When made by this process, the trichloride is contaminated with the pentachloride. Different ways of preparing the trichloride by the action of chlorine on yellow or red phosphorus have been devised by J. B. A. Dumas, V. Rekschinsky, C. Gräbe, A. A. Vanscheidt and V. M. Tolstopiatoff, etc.

> A layer of sand is placed at the bottom of a retort, and a current of dry carbon dioxide, or other inert gas, passed through the retort. Add, say, 100 grms. of yellow phosphorus —dried between filter-paper, and dipped successively in alcohol and in ether—then pass a current of chlorine through the apparatus while tho retort is heated with warm water. The tube delivering the chlorine should be movable, for if it is too near the phosphorus the phosphorus becomes hot and distils, forming a red crust in the upper part of the retort; while if it be too far away the action is slow, and the excess of phosphorus forms phosphorus pentachloride by a side reaction. When the action has begun, a tongue of flame projects from the tube delivering the chlorine. The retort does not then need heating. Towards the end, when the phosphorus has all disappeared, heat the retort very gently so as to drive the trichloride into the receiver. The fumes from the exit tube must be led into a stink closet or into a vessel containing sodium hydroxide. The product can be purified by adding, say, 2 grms. of yellow phosphorus and redistilling. The object of the phosphorus is to convert any pentachloride into the trichloride. J. J. Berzelius, and P. L. Dulong recommended a second distillation to remove the excess of phosphorus. Moisture must be carefully excluded.

U. J. J. Leverrier found that the trichloride is produced by the action of chlorine on phosphorus tetritoxide; and A. Besson, on phosphorus hemioxide; T. E. Thorpe and A. E. H. Tutton obtained it by the action of phosphorus pentachloride or of hydrogen chloride on phosphorous oxide: $P_4O_6+6PCl_5=6POCl_3+4PCl_3$; and $P_4O_6+6HCl=2PCl_3+2H_3PO_3$. A. Oppenheim found that it is produced when conc. hydrochloric acid is heated with phosphorus in a sealed tube at 200°: $2P+3HCl=PH_3+PCl_3$. H. Davy, and J. L. Gay Lussac and L. J. Thénard made the trichloride by passing the vapour of phosphorus over heated mercurous or mercuric chloride; and J. H. Gladstone added that a similar result is obtained with ferric and cupric chlorides, but not with lead chloride. H. F. Gaultier de Claubry observed that the trichloride is formed when sulphur monochloride is passed over phosphorus, the sulphur is set free; E. Baudrimont observed that a similar reaction occurs with selenium mono- or tetra-chloride; and P. Köchlin and K. Heumann, by the action of phosphorus on pyrosulphuryl chloride—they recommended heating sulphuryl chloride with red phosphorus in a flask fitted with a reflux condenser as a mode of preparing phosphorus trichloride: $3SO_2Cl_2+2P=2PCl_3+3SO_2$. P. P. Budnikoff and E. A. Shiloff found that calcium phosphate can be almost quantitatively converted into phosphorus trichloride by heating it with silica and charcoal as catalyst, in a current of sulphur monochloride: $4S_2Cl_2+Ca(PO_3)_2=2PCl_3+CaCl_2+3SO_2+5S$. Some silicon tetrachloride, derived from the silica, may be present.

The trichloride is formed by quite a number of metathetical reactions. In illustration, J. H. Gladstone showed that it is produced by the action of chlorine, or mercuric chloride on phosphorus tribromide or triiodide; A. Gautier, by the action of phosphorus diiodide on silver chloride: $3PI_2+6AgCl=6AgI+P+2PCl_3$; and C. Poulenc, by warming at 120° phosphorus with the dichlorotrifluoride: $3PF_3Cl_2+2P=3PF_3+2PCl_3$. J. L. Gay Lussac and L. J. Thénard said that a little trichloride is formed when glacial phosphoric acid is heated with sodium chloride; and H. Rose, when sodium hydrophosphate is heated with ammonium chloride. The trichloride is produced during the thermal dissociation of phosphorus pentachloride, and when the pentachloride is reduced by many metals, hydrogen, phosphine, etc.—*vide infra*, phosphorus pentachloride. J. Riban obtained the trichloride by reducing phosphoryl chloride with red-hot wood-charcoal; $POCl_3+C=CO+PCl_3$.

The physical properties of phosphorus trichloride.—At ordinary temp., phosphorus trichloride is a transparent, colourless, mobile, fuming liquid. H. V. Regnault[3] gave 4·7464 for the **vapour density** of phosphorus trichloride, and J. B. A. Dumas, 4·75, air unity. H. Davy's value, 1·45, for the **specific gravity** is low; H. L. Buff gave 1·6119 at 0°, 1·5971 at 10°, and 1·4712 at 76°; J. I. Pierre, 1·6162 at 0°; W. Ramsay and J. Shields found 1·5825 at 16·4°; and 1·527 at 46·2°; and G. Carrara and I. Zoppelari, 1·5941 at 11°/4°; A. Stiefelhagen, 1·613 at 18°; T. E. Thorpe, 1·61275 and 1·61294 at 94°, and 1·46845 at 75·95°. J. Timmermans estimated that the sp. gr. of the liquid at —273° is 2·11927; and at higher temp., T° K., $D=2{\cdot}11927-0{\cdot}00189994T+0{\cdot}0_6 1183T^2$. F. M. Jäger's values are indicated below. J. I. Pierre represented the volume, v, at θ° between —35° and 74·9° by $v=1+0{\cdot}001128620\theta+0{\cdot}0_6 87288\theta^2+0{\cdot}0_7 179236\theta^3$; and T. E. Thorpe, by $v=1+0{\cdot}001139370\theta+0{\cdot}0_5 166807\theta^2+0{\cdot}0_8 4012\theta^3$—when the vol. at 0° is unity. The vol. at 75·95° is 1·09827 when the vol. at 0° is unity. H. Kopp found **molecular volume** at the b.p. to be 93·9; H. L. Buff, 93·01–93·62; E. B. R. Prideaux, 93·34; E. Rabinowitsch, 93·7; and T. E. Thorpe, 93·34–93·68. A. Masson, S. Sugden, and J. A. Groshans studied the mol. vols. of the family of halides; and F. Ephraim calculated that a 10 per cent. expansion occurs during the formation of the trichloride. I. I. Saslowsky studied the contraction during the formation of the halide from its elements. K. M. Stakhorsky studied the mol. association of the liquid. E. H. Amagat found the **compressibility** coeff. of the liquid at 10·1° to be $0{\cdot}0_4 72$ between 1 and 500 atm. press.; $0{\cdot}0_4 54$ between 500 and 100 atm.; $0{\cdot}0_4 45$ between 1000 and 1500 atm.; $0{\cdot}0_4 38$ between 1500 and 2000 atm.; $0{\cdot}0_4 33$ between 2000 and 2500 atm.; and $0{\cdot}0_4 29$ between 2500 and 3000 atm. P. W. Bridgman found the following relations between the press., p kgrm. per sq. cm., and the vol. of the liquid:

p . .	1	500	1000	2500	5000	8000	10,000	12,000
v 20° .	1·0234	0·9862	0·9593	0·9057	0·8521	0·8133	0·7929	0·7763
40° .	1·0485	1·0040	0·9739	0·9159	0·8600	0·8196	0·7989	0·7818
60° .	1·0752	1·0238	0·9896	0·9268	0·8682	0·8260	0·8050	0·7875
80° .	1·1039	1·0459	1·0065	0·9375	0·8757	0·8323	0·8109	0·7928

T. W. Richards represented the *vp*-curve of a millilitre of the trichloride up to 12,000 atm. by $p+6200(v-0{\cdot}67)=2050$. W. Ramsay and J. Shields found the **surface tension** of the liquid to be 28·71 dynes per cm. at 16·4°, and 24·91 dynes per cm. at 46·2° ; and the values for the **specific cohesion** are respectively $a^2=3{\cdot}49$ and $a^2=3{\cdot}32$ sq. mm. ; and the mol. **surface energy** at 16·4° is 562·3 ergs and at 46·2°, 499·8 ergs. P. Walden gave 0·00414 for the temp. coeff. of the surface tension, and for the sp. cohesion at $\theta°$, $a^2=4{\cdot}05(1-0{\cdot}000338\theta)$. F. M. Jäger found the sp. gr. referred to water at 4°, the specific cohesion a^2 in sq. mm., the surface tension, σ, in dynes per cm., and the mol. surface energy, μ, in ergs per sq. cm. :

	−70°	−20·5°	0°	35·2°	64·8°	75·1°
Sp. gr. . .	1·744	1·653	1·613	1·547	1·492	1·475
a^2 . . .	4·37	3·90	3·70	3·40	3·13	3·03
σ . . .	37·4	31·6	29·3	25·8	22·9	21·9
μ . . .	687·4	601·9	567·3	513·6	467·0	450·1

R. Lorenz and W. Herz studied some relations of the surface tensions of the family of halides. N. de Kolossowsky studied the relation between the capillary constants and the heat of vaporization.

The mean coeff. of **thermal expansion** of the gas given by L. Troost and P. Hautefeuille is 0·00489 at 100°–125° ; and 0·00417 at 125°–180°. J. I. Pierre gave 0·001154 for the coeff. of cubical expansion of the liquid between —36° and 75° ; T. E. Thorpe, 0·001211 between 0° and 75° ; and P. Walden, 0·00117 between 0° and 60°. I. I. Saslowsky studied the relation between the coeff. of expansion and the chemical structure. H. V. Regnault found 0·1346 to 0·1347 for the **specific heat** of the vapour at constant press. between 111° and 246°. The **vapour pressure,** p mm., of the liquid found by H. V. Regnault is :

	−20°	−10°	0°	10°	20°	30°	40°	50°
p . . .	37·98	62·88	100·55	155·65	233·78	341·39	485·63	674·33

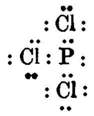
The results were represented by $\log p=4{\cdot}7479108-3{\cdot}1684558a^{\theta}$, where $\log a=\bar{1}{\cdot}9968895$; and C. Antoine gave $\log p=1{\cdot}2112\{5{\cdot}6885-1000(\theta+228)^{-1}\}$. P. de Mondesir also made observations on this subject. F. M. Raoult measured the lowering of the vap. press. by organic substances dissolved in the trichloride. The **boiling point** found by J. B. A. Dumas was between 76° and 78° ; H. V. Regnault gave 73·8° at 760° ; H. L. Buff, 76° ; P. Köchlin and K. Heumann, 75° ; B. Pawlewsky, 75·5° ; H. Kopp, and L. Troost and P. Hautefeuille, 78° ; A. Haagen, 76·7° at 745·9 mm. ; J. I. Pierre, 78·3° at 751·5 mm. ; T. Andrews, 78·5° at 767 mm. ; F. M. Jäger, 75° at 749 mm. ; P. Walden, 76°–76·3° at 763 ; and T. E. Thorpe, 75·95° at 760 mm., and 76·25° at 768 mm. N. de Kolossowsky gave 4·36 to 4·67 for the **ebulliscopic constant.** H. V. Regnault gave 67·24 Cals. for the **heat of vaporization** per kilogram, and 9·25 Cals. per mol. ; and T. Andrews gave respectively 51·42 Cals. and 7·1 Cals. at 78·5°. J. Natterer found that the liquid does not freeze at —115°, but S. A. von Wroblewsky and K. Olschewsky gave about —111·5° for the **melting point ;** and F. M. Jäger, —90°. G. N. Huntly found that a mol of phosphorus trichloride dissolved in 100 mols of phosphoryl chloride lowers the f.p. 0·48°—F. M. Raoult gave 0·63° ; and S. U. Pickering found that with benzene as solvent, the molar depression was 0·6305° to 0·6382°. B. Pawlewsky found the **critical temperature** to be 285·5°, and W. Ramsay and J. Shields, 290·5°. L. Kahlenberg and A. T. Lincoln measured the lowering of the f.p. of soln. of phosphorus trichloride in nitrobenzene. N. de Kolossowsky studied the relation between the coeff. of expansion and the latent heat of vaporization.

B. H. Wilsden studied the energy involved in the electronic shifts during the dissociation of phosphorus trichloride. J. Thomsen found for the **heat of formation** of the liquid trichloride (P,3Cl)=75·3 Cals. ; M. Berthelot and W. Louguinine, 76·6 Cals. ; and J. Ogier, 75·8 Cals. J. Thomsen gave 65·14 Cals. for the **heat of solution** of a mol of the trichloride in 1000 mols of water ; M. Berthelot and W. Longuinine found that one eq. of phosphorus trichloride develops 63·3 Cals.

when treated with about 100 times its weight of water; with a soln. of potassium hydroxide (1 : 50), 132·4 Cals. Observations were also made by P. A. Favre and J. T. Silbermann, H. W. Schröder van der Kolk, and J. Thomlinson.

E. Mascart found the **index of refraction** of phosphorus trichloride vapour to be 1·0001740 for Na-light. F. F. Martins, and J. H. Gladstone and T. P. Dale measured the index of refraction of the liquid trichloride, and A. Stiefelhagen gave for light of wave length $\lambda=263$, 394, and $768\mu\mu$, the index $\mu=1{\cdot}664$, 1·54274, and 1·50340, and $\mu^2=1{\cdot}63317+0{\cdot}59309\lambda^2(\lambda^2-178{\cdot}82^2)^{-1}$. A. Haagen gave for the **refraction equivalent,** 44·3. W. A. Miller said that the colourless liquid absorbs completely the so-called chemical rays of the spectrum. C. R. Crymble measured the absorption spectrum of the trichloride. J. E. Purvis observed no absorption bands in the ultra-violet. H. Davy found the liquid is a non-conductor of electricity; and P. Walden, and A. Voigt and W. Biltz said that at 25° the **electrical conductivity** of the liquid is almost zero—*vide infra,* phosphorus pentachloride. L. Kahlenberg and A. T. Lincoln found the mol. electrical conductivity in ethyl acetoacetate to be $\mu_{1\cdot80}=0{\cdot}026$; and $\mu_{4\cdot48}=0{\cdot}097$; and in nitrobenzene, $\mu_{8\cdot43}=0{\cdot}026$, and $\mu_{16\cdot86}=0{\cdot}042$. W. Finkelstein found the **decomposition voltage** in nitrobenzene soln. to be 0·82 volt. H. Schlundt gave 3·72 for the dielectric constant at 18°; and P. Walden, 4·7 at 22°. A. Bertin found the coefficient of **magnetic polarization** to be 0·51 when that of flint glass is unity.

The analyses of H. Davy, J. J. Berzelius, J. B. A. Dumas, and P. Köchlin and K. Heumann agree with the empirical formula PCl_3; the vap. density determinations of H. V. Regnault, and J. B. A. Dumas agree with the mol. formula PCl_3. This result is also in harmony with the state of the chloride in benzene and phosphoryl chloride soln. determined by G. N. Huntly, and S. U. Pickering; and W. Ramsay and J. Shields, determinations of the surface energy agree that the mol. wt. of the liquid and gas is the same because the association factor is only 1·02. H. Henstock discussed the electronic structure; and G. W. F. Holroyd gave



$$\begin{array}{rl} & :\ddot{\mathrm{Cl}}: \\ :\ddot{\mathrm{Cl}}: & \ddot{\mathrm{P}}: \\ {}^{\bullet\bullet} & :\underset{\bullet\bullet}{\ddot{\mathrm{Cl}}}: \end{array}$$

The chemical properties of phosphorus trichloride.—H. Davy[4] likened the odour of phosphorus trichloride to that of hydrochloric acid; and he said that the liquid has no action on litmus. P. W. Butjagin found that air with 0·004 mgrm. of the trichloride per litre produced very slight symptoms of a disturbance in 6 hrs.; air with 3 mgrms. per litre caused the death of animals in 3 hrs. As indicated above, A. Besson and A. Fournier showed that when a mixture of **hydrogen** and phosphorus trichloride is subjected to the silent electric discharge, phosphorus dichloride is formed. H. Davy said that the vapour burns in the flame of a candle. A. Michaelis said that at ordinary temp. phosphorus trichloride shows no very marked affinity for **oxygen,** but it does so at a higher temp. According to W. Odling, phosphorus trichloride absorbs oxygen at ordinary temp., and is thereby transformed into the oxychloride; and A. Michaelis said that the oxidation is very incomplete even after boiling for 3 days. W. D. Bancroft and H. B. Weiser found that when a cold surface is placed in a flame fed with phosphorus trichloride, a dull deposit of red phosphorus is formed. I. Remsen said that **ozone** transforms the trichloride into the oxychloride. H. Davy said that the trichloride reacts with **water** with a rise of temp. and the gradual formation of hydrochloric and phosphorous acids: $PCl_3+3H_2O=H_3PO_3+3HCl$. M. Trautz observed no signs of luminescence during the reaction between phosphorus trichloride and hot or cold water. K. Kraut observed that if water insufficient for the complete reaction is added to phosphorus trichloride, some red phosphorus and phosphoric acid may be formed: $5PCl_3+12H_2O=3H_3PO_4+15HCl+2P$; and he thought that the phosphorous acid first formed reacts with the phosphorus trichloride: $PCl_3+4H_3PO_3$

$=3H_3PO_4+3HCl+2P$; whereas A. Geuther represents the reaction: $4H_3PO_3=3H_3PO_4+PH_3$; and $PCl_3+PH_3=2P+3HCl$. A. Geuther said that the separation of phosphorus occurs only with impure trichloride and that the alleged phosphorus is really arsenic derived from the arsenic chloride contamination. A. Besson found that when a small proportion of water is used, some phosphoryl monochloride may be formed. The reaction was also studied by A. Michaelis; and G. Carrara and I. Zoppelari found that the progress of decomposition in the heterogeneous system: water-phosphorus trichloride can be represented by $(1/aSt)\log a/(a-x)=k$, where S represents the surface area of the liquids in contact; a, the quantity of decomposable liquid; x, the quantity of liquid decomposed at the time t; and k is the velocity constant 0·000297. According to A. D. Mitchell, when phosphorus trichloride is hydrolyzed by water the soln. produced has much stronger reducing properties when first formed than has a normally produced soln. of phosphorous acid; its acidity is 98 per cent. of the theoretical at first, and gradually increases during ½ hr. to the maximum, probably owing to the intermediate formation and gradual decomposition of an oxychloride. The duration of increased reducing power is greater than can be attributed to the formation of the oxychloride, and is most probably due to the presence of the active tautomeric form of phosphorous acid, $P(OH)_3$, which is slowly converted into the normal form $HPO(OH)_2$. N. V. Sidgwick discussed the nature of the first attack by water on the trichloride.

H. Moissan said that phosphorus trichloride reacts with **fluorine** with incandescence, forming chlorine and the pentafluoride. It was shown by F. Donny and J. Mareska, J. B. A. Dumas, J. Personne, and A. Schrötter, that **chlorine** converts the trichloride into the pentachloride (*q.v.*). H. Wichelhaus said that **bromine** forms a compound with the trichloride only in the cold; A. Michaelis, and A. Prinvault said that reaction occurs at ordinary and at elevated temp. A. L. Stern found a progressive substitution and addition of bromine when the proportion of bromine and the temp. are varied. C. A. Wurtz said that **iodine** does not react with the trichloride; and J. H. Gladstone, that iodine dissolves in the liquid without forming a compound. H. Ritter said that a soln. of iodine in acetic acid forms phosphorus diiodide. C. G. Moot showed that if the soln. of iodine in phosphorus trichloride is allowed to stand for some time, brown trichlorodiiodide is formed. J. H. Gladstone observed that liquid bromine sinks in liquid phosphorus trichloride without mixing, but if a little iodine is added, a vigorous reaction accompanied by the development of heat sets in: $PCl_3+I+5Br=PBr_5+ICl_3$. E. Baudrimont said that the trichloride reacts with **iodine pentabromide,** forming phosphorus triiodide and pentabromide. A. Besson obtained the tribromide by the action of **hydrogen bromide** on the trichloride, although some chlorobromide may be formed. P. Hautefeuille said that when the trichloride is heated with **hydrogen iodide,** hydrogen chloride and phosphorus triiodide are produced. H. L. Snape found that the trichloride is not attacked by **potassium bromide** if oxygen and moisture be excluded, while **potassium iodide** furnishes phosphorus iodide. E. Dervin said that there is a vigorous reaction with **potassium chlorate:** $3PCl_3+KClO_3=3POCl_3+KCl$.

J. H. Gladstone said that **sulphur** does not react with phosphorus trichloride at the b.p., about 78°, but at 140°, L. Henry found that thiophosphoryl chloride is formed. U. Antony and G. Magri showed that phosphorus trichloride dissolves in liquid **hydrogen sulphide,** forming a colourless liquid; there is a rise of temp. during the dissolution, 100 c.c. of the liquid sulphide dissolving 0·11 grm. of the trichloride, and the soln. is an electrical conductor. G. S. Sérullas, and E. Baudrimont found that gaseous hydrogen sulphide reacts with the liquid, forming phosphorus sulphide and hydrogen chloride. W. Biltz and E. Keunecke found that dry, liquid hydrogen sulphide dissolves phosphorus trichloride without the vap. press. of the soln. curve showing any discontinuity; and G. N. Gaum and J. A. Wilkinson found that the soln. are electrical conductors. According to A. Michaelis, **sulphur dioxide** mixes with phosphorus trichloride, but there is no chemical action, even at 140°; when passed through a red-hot tube, the mixed vapours form sulphur, and phosphoryl and thiophosphoryl chlorides. H. E. Armstrong, and A. Michaelis observed that the trichloride reacts vigorously with **sulphur trioxide,** forming sulphur dioxide and phosphoryl chloride—the former observed that a by-product, possibly phosphorus dioxymonochloride, is formed. H. Rose also studied this reaction. A. Michaelis found that conc. **sulphuric acid** on standing in contact with the trichloride reacts: $2PCl_3+3H_2SO_4=2SO_2+P_2O_5+5HCl+HSO_3Cl$; but A. Geuther symbolized the reaction: $PCl_3+2H_2SO_4=SO_2+2HCl+HPO_3+HSO_3Cl$. A. Michaelis found that when the trichloride is heated at 160° with **sulphur monochloride,** the reaction is symbolized: $3PCl_3+S_2Cl_2=PCl_5+2PSCl_3$; and with **thionyl chloride:** $3PCl_3+SOCl_2=PCl_5+POCl_3+PSCl_3$; he also found that in the cold **chlorosulphonic acid** produces sulphur dioxide and hydrogen chloride, a reaction symbolized by A. Geuther: $PCl_3+HSO_3Cl=POCl_3+SO_2+HCl$. A. Michaelis found that **pyrosulphuryl chloride** reacts in the cold, forming phosphorus pentachloride, phosphoryl chloride, and sulphur dioxide. A. Michaelis said that some heat is developed when **selenium dioxide** is mixed in the cold with phosphorus trichloride, and the mixture becomes red-hot; if heated in a sealed tube at 100°–110°, the reaction is symbolized $SeO_2+2PCl_3=Se+2POCl_3$; and when **selenyl chloride** is mixed with the trichloride, some heat is developed, and the reaction is symbolized: $3PCl_3+3SeOCl_2=SeCl_4+Se_2Cl_2+3POCl_3$. E. Baudrimont symbolized the reaction with **selenium tetrachloride**: $6PCl_3+7SeCl_4=3(PCl_5)_2SeCl_4+2Se_2Cl_2$. V. Lenher found that **tellurium dioxide** is reduced to tellurium.

E. A. Schneider found that when passed over **magnesium nitride** at a red-heat, a mixture of the vapour of phosphorus trichloride and nitrogen forms no phosphorus nitride. H. Perpérot found that by mixing soln. of ammonia and of phosphorus trichloride in carbon tetrachloride, impure **phosphorus hexamminotrichloride,** $PCl_3.6NH_3$, is formed, and he represented the reactions with the tri-, penta-, or oxychloride as involving the primary reaction: $PCl_n+2nNH_3=PCl_n.2nNH_3$ and $PCl_n.2nNH_3=nNH_4Cl+P(NH_2)_n$. There is a break on the time-decomposition curve at 200°. J. Perzoz also obtained **phosphorus octamminotrichloride,** $PCl_3.8NH_3$. A. Michaelis and A. Geuther found that **nitrogen peroxide** reacts slowly with well-cooled phosphorus trichloride, forming pyrophosphoryl chloride, phosphoryl chloride, phosphorus pentoxide, nitrosyl chloride, nitrogen, and nitric oxide; and J. Perzoz and N. Bloch said that an explosion occurs when the trichloride is brought in contact with **nitrous acid** or with **nitric acid.** H. Davy said that warm phosphorus trichloride dissolves a little phosphorus, and when the soln. is exposed to air, it deposits a film of **phosphorus**; while paper moistened with the soln. takes fire in air as soon as the liquid has evaporated; if the soln. be exposed to air in daylight, hydrated phosphoric acid is deposited; and, according to U. J. J. Leverrier, in sunlight, phosphorus tetritoxide is deposited. J. J. Berzelius said that when the soln. is treated with water it forms hydrochloric and phosphorous acids with the deposition of clear, transparent phosphorus. H. Rose, and R. Mahn found that the trichloride reacts with **phosphine,** forming hydrogen chloride and phosphorus; A. Besson said that hydrogen diphosphide not phosphorus is produced; and P. de Wilde found that purified phosphine reacts only slowly, and that **hydrogen hemiphosphide** vapour reacts producing hydrogen chloride and hydrogen diphosphide, not phosphorus; **phosphonium iodide** reacts with the trichloride, forming hydrogen chloride, phosphine, hydrogen diphosphide, and phosphorus diiodide. A. Michaelis and M. Pitsch represented the reaction with **hypophosphorous** acid: $4H_3PO_2+2PCl_3=P_4O+H_3PO_3+H_3PO_4+6HCl$. A. Geuther gave $3H_3PO_2+PCl_3=2H_3PO_3+2P+3HCl$. T. E. Thorpe and A. E. H. Tutton found that **phosphorous oxide** has scarcely any action on the trichloride at ordinary temp., or at the b.p., but at 180°, $5P_4O_6+5PCl_3=3PCl_5+6P_2O_5+10P$. A. Naquet found that with **phosphorous acid,** phosphorous oxide is formed; and A. Besson represented the reaction with a conc. soln. of phosphorous acid: $2H_3PO_3+2PCl_3=6HCl+P_4O_6$, and $P_4O_6=P_2O+P_2O_5$. When the trichloride is heated with **phosphoric acid** on a water-bath, A. Geuther symbolized the reaction: $3H_3PO_4+PCl_3=3HPO_3+H_3PO_3+3HCl$; followed by a reaction between the trichloride and the phosphorous acid producing metaphosphoric and pyrophosphoric acids. He symbolized the reaction with **pyrophosphoric acid**: $3H_4P_2O_7+PCl_3=6HPO_3+H_3PO_3+3HCl$, along with the formation of some red phosphorus. According to F. Krafft and R. Neumann, **arsenic** and phosphorus trichloride do not react at 320°, but if a little arsenic chloride be present, the reaction is almost quantitative at 200°. J. V. Janowsky symbolized the reaction with **arsine**: $AsH_3+PCl_3=PAs+3HCl$. A. Michaelis found that **arsenic trioxide** is reduced to arsenic at 100°, and at 130°, he symbolized the reaction: $5As_2O_3+6PCl_3=4As+6AsCl_3+3P_2O_5$; but **arsenic pentoxide** does not react with the trichloride at 200°. H. Moissan observed that with **arsenic trifluoride,** some dark brown arsenic is formed. A. W. Cronander obtained a crystalline mass of *arsenic phosphoctochloride,* $AsCl_5.PCl_3$, by dissolving phosphorus pentachloride in arsenic trichloride. E. Beckmann said that **arsenic triiodide** is sparingly soluble in phosphorus trichloride, while P. Walden found the dried **arsenic trihalides** to be all fairly soluble in that menstruum. E. Baudrimont showed that heated **antimony** reacts with phosphorus trichloride, forming antimony trichloride and phosphorus; and F. Krafft and R. Neumann studied the reaction at 200°. R. Mahn said that **stibine** does not react with phosphorus trichloride. A. Michaelis said that the trichloride reacts with **antimony trioxide**, producing red phosphorus and antimony trichloride; and with **antimony pentoxide** the reaction is symbolized: $Sb_2O_5+2PCl_3=2SbCl_3+P_2O_5$. E. Beckmann said that antimony triiodide is sparingly soluble in phosphorus trichloride, but P. Walden said that antimony trihalides are all fairly soluble. H. A. Köhler observed that phosphorus trichloride reacts with **antimony pentachloride,** forming a complex $2SbCl_5+PCl_3=SbCl_3+PCl_5.SbCl_5$. A. Michaelis showed that **bismuth** forms a little phosphorus when heated with phosphorus trichloride; and at 160°, in a sealed tube, **bismuth oxide** reacts with phosphorus trichloride, forming bismuth dichloride and phosphate, and bismuthyl and phosphoryl chlorides. F. E. Brown and J. E. Snyder observed that **vanadium oxytrichloride** is reduced by phosphorus trichloride, forming a precipitate.

G. Gustavson observed no reaction with **boron trioxide** when heated with phosphorus trichloride for 2 weeks at 200°; J. Tarible showed that with **boron tribromide,** a complex *boron phosphohexabromotrichloride,* $2BBr_3.PCl_3$, is formed. Phosphorus trichloride reacts with numerous **organic compounds**—alcohols, acid anhydrides, acids, etc.—forming chlorides. It is an important reagent in many organic syntheses. A. G. Page discussed its use as a catalyst in organic chlorinations. This subject was also discussed by Lassar Cohn. Phosphorus trichloride is used as a reagent for replacing hydroxyl groups by chlorine. It was first employed for this purpose by A. Béchamp in 1856, who found that **acetic acid,** CH_3COOH, could be converted into acetyl chloride, CH_3COCl, by a reaction symbolized: $3CH_3COOH+PCl_3=H_3PO_3+3CH_3COCl$. This principle is applied in determining the number of hydroxyl groups in acids—*e.g.* sulphurous and sulphuric acids. Many of the oxy-halides can be regarded as products obtained by replacing the HO-group in the acid by chloride—*e.g.* $(HO)_4P_2O_3$, pyrophosphoric acid furnishes pyrophosphoryl chloride, $P_2O_3Cl_4$. The action of phosphorus trichloride on the aliphatic **alcohols** was studied by A. Béchamp, and T. Milobendzky and A. Sachnowsky. The first product of the reaction is the normal phosphorous ester which is decomposed by the liberated hydrogen chloride into acid ester and alkyl chloride. J. W. Walker and F. M. G. Johnson represented the reaction with methyl, ethyl, and *n*-propyl alcohols by the typical equation: $PCl_3+3CH_3OH=2CH_3Cl+HCl+P(OH)_2(OCH_3)$. V. Auger found that phosphorus trichloride reacts at −20° with **methyl, ethyl, or propyl iodide** to form alkyl phosphines. B. T. Brooks found that when acetic acid reacts with phosphorus trichloride, in addition to acetyl chloride there are simultaneously formed small quantities of acetyl anhydride and of *acetyl phosphorous acid,* $(CH_3CO.O)P(OH)_2$. P. Carré found that the trichloride reacts with **glycerol**, and with **glycol**; in the former case, phosphorous esters are formed. P. Walden found the trichloride to be a good solvent for numerous organic compounds, but not for many inorganic compounds. R. Mahn said that **silane** was not perceptibly affected by phosphorus trichloride. A. Bertrand obtained with **titanium tetrachloride** the complex *titanium phosphoheptachloride*, $TiCl_4.PCl_3$, in crystals melting at 85·5°. T. Karantassis observed that phosphorus trichloride undergoes double decomposition with **titanium tetraiodide**, but the reverse reaction does not occur even in sealed tubes at 200°. It is concluded that the chlorides of the tervalent metalloids undergo double decomposition with the **iodides of carbon, silicon, titanium, zirconium, thorium, germanium, and hafnium**, but do not react with **stannic chloride.**

H. Davy said that **potassium** burns vigorously in the vapour of phosphorus trichloride, and J. H. Gladstone observed that the trichloride sets fire to potassium. H. Beutler and M. Polanyi observed chemiluminescence in the reaction with **sodium**; and V. C. Vournasos represented the reaction with heated sodium: $PCl_3+6Na=3NaCl+Na_3P$; and in boiling toluene soln., potassium furnishes potassium chloride and phosphide. According to A. Granger, when the vapour of the trichloride is passed over heated **copper**, or when copper is heated with the trichloride, crystalline copper diphosphide is formed; L. Wolf also studied this reaction. According to J. H. Gladstone, the liquid trichloride does not react with **silver**, but after shaking the mixture 2 weeks at 100°, L. Wolf found the reaction: $PCl_3+3Ag=3AgCl+P$ occurred. L. Wolf found that phosphorus trichloride has only a slight action on **magnesium**. W. T. Casselmann, L. Wolf, and B. Reinitzer and H. Goldschmidt found that with **zinc** at 100°, zinc chloride and phosphorus are formed; and G. Denigès said that dry zinc powder does not act on the liquid. L. Wolf represented the reaction which occurs when **mercury** is shaken a long time with phosphorus trichloride as forming mercury and mercurous chloride; and with **aluminium** at 100°, $PCl_3+Al=AlCl_3+P$. J. L. Gay Lussac and L. J. Thénard said that when the trichloride is heated with **iron** filings, ferric chloride and iron phosphide are formed—A. Granger represented the phosphide so produced by Fe_4P_3; and for the corresponding case with **nickel**, Ni_5P_2, and later, Ni_2P; and with **cobalt** at 500°, Co_2P.

A. Michaelis represented the reaction with **copper oxide**, $17CuO+5PCl_3=2Cu_3(PO_4)_2+10CuCl+CuCl_2+POCl_3$; and with mercury oxide he employed an analogous equation. At 160°, **stannic oxide** reacts: $5SnO_2+4PCl_3=4SnCl_2+SnCl_4+2P_2O_5$; and W. T. Casselmann obtained no complex with **stannous chloride**; **lead oxide** does not react at 160°, but at higher temp., $6PbO+2PCl_3=Pb(PO_3)_2+3PbCl_2+2Pb$; and with **lead dioxide**, $4PbO_2+4PCl_3=Pb(PO_3)_2+3PbCl_2+2POCl_3$; A. Michaelis said that phosphorus trichloride reacts with **potassium dichromate**: $30K_2Cr_2O_7+42PCl_3=18KCrO_3Cl+15KPO_3+42CrO_2+27KCl+27POCl_3$; with **chromyl chloride**: $4CrO_2Cl_2+6PCl_3=4CrCl_3+PCl_5+3POCl_3+P_2O_5$; or $6CrO_2Cl_2+9PCl_3=6CrCl_3+7POCl_3+P_2O_5$; H. S. Fry and J. L. Donnelly said that the violence of the reaction can be moderated in soln. of dry carbon tetrachloride when a complex *chromyl phosphoryltetrachloride*, $CrOCl.POCl_3$, is formed. It is decomposed by water. According to A. Michaelis, phosphorus trichloride produces only a superficial green film on **tungsten trioxide** at 200°; and with **molybdenum trioxide**, a superficial blue film; but in a sealed tube at 160°: $MoO_3+PCl_3=MoO_2+POCl_3$, followed by $3MoO_3+2POCl_3=3MoO_2Cl_2+P_2O_5$; **manganese dioxide**, and **ferric oxide** are not attacked. E. Baudrimont found that with **potassium, calcium, or barium sulphide**, at a red-heat, the corresponding chloride and phosphorus sesquisulphide are formed; with **mercuric sulphide**, both mercuric and mercurous chlorides are formed as well as mercury thiophosphide, and if the phosphorus chloride is in excess, phosphorus sesquisulphide is produced. At a red-heat, **antimony trisulphide** forms antimony trichloride and phosphorus sesquisulphide—and may be a red antimony thiophosphide. The action on **lead sulphide** is similar. L. Wolf found **cuprous chloride** furnishes **dicuprous phospho-**

pentachloride, and a similar product is obtained with **cuprous bromide**; no addition product is formed with **silver chloride or bromide.** Phosphorus trichloride was found by H. Moissan to react with **silver fluoride,** forming phosphorus trifluoride. L. Wolf observed the formation of no complex salt between phosphorus trichloride and **mercury chloride or bromide,** but H. Moissan found that the trichloride forms a complex with **zinc fluoride,** and, according to A. Guntz, with **lead fluoride.** L. Lindet obtained complex salts with **aurous chloride** and **aurous bromide,** namely, **aurous phosphotrichlorobromide,** $AuBr.PCl_3$, and **aurous phosphotetrachloride,** $AuCl.PCl_3$. M. Levi-Malvano added phosphorus trichloride to a soln. of **auric chloride** in ether and obtained **auric phosphohexachloride,** $AuCl_3.PCl_3$. P. Schützenberger also obtained with **platinous chloride,** the complex **platinous phosphopentachloride,** $PtCl_2.PCl_3$; and P. Schützenberger and M. Fontaine, **platinous diphosphoroctochloride,** $PtCl_2.2PCl_3$; G. Geisenheimer, and M. F. Schurigin, **iridium triphosphododecachloride,** $Ir(PCl_3)_3Cl_3$; and G. Geisenheimer **iridium triphosphopentadecachloride,** IrP_3Cl_{15}, but M. F. Schurigin could not make this. E. Fink obtained **palladous phosphopentachloride,** $PdCl_2.PCl_3$, and **palladous phosphoctochloride,** $PdCl_2.2PCl_3$; and M. F. Schurigen obtained **ruthenic pentaphosphoenneadecachloride,** $Ru_2(PCl_3)_5Cl_4$. M. F. Schurigen represented the constitution of these products by the co-ordination formulæ with phosphorus trichloride taking the place of ammonia in the ammines.

P. Biginelli[5] observed that phosphine unites with mercuric chloride to form a yellow mass; and P. Lemoult observed the formation of an unstable intermediate product when phosphine acts on an aq. soln. of mercuric chloride and potassium chloride. If the gas be confined over the liquid and suddenly shaken, the resulting yellow precipitate can be dried in vacuo over sulphuric acid. Its composition corresponds with **phosphorus triochloromercuriate,** $P(HgCl)_3$, or $HgCl_2.PHg_2Cl$. H. Rose obtained a product approximating to a *hemitrihydrate* by the action of phosphine on an aq. or alcoholic soln. of mercuric chloride. A. Partheil and A. van Haaren worked with an alcoholic soln. and said that the phosphine should be diluted with an inert gas. D. Vitali obtained a similar substance. The yellow product is decomposed by heat; by boiling water; conc. alkali-lye; hydrogen sulphide; and by dil. nitric acid. For analogous reactions with mercuric bromide and iodide, *vide infra.*

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§ 32. Phosphorus Pentachloride or Phosphoric Chloride

As previously indicated, this compound is formed as a white solid when phosphorus is burnt in contact with an excess of chlorine. It was first made by H. Davy[1] in this way in 1810, but its nature was not definitely established until 1816, when P. L. Dulong's analysis, translated into modern symbols, showed it to possess the ultimate composition PCl_5. It was also analyzed by J. J. Berzelius, W. T. Casselmann, and E. B. R. Prideaux. The vapour density presents an anomaly. The theoretical value, according to Avogadro's law, is 7·22, the value observed by A. Cahours is 5·08 at 182°, and at temp. exceeding 300°, it has the constant value 3·65, which is about half what was anticipated. In the struggle of Avogadro's hypothesis for recognition (**1.** 5, 7), the advocates of the atomic theory attributed the anomaly to the dissociation of the molecule with rise of temp., $PCl_5 \rightleftharpoons PCl_3 + Cl_2$. This stimulated quite a number of observations on the subject. The general results show that phosphorus pentachloride is only partially dissociated at the lower temp. of observation employed by A. Cahours, and that dissociation is complete above 300°. When due allowance is made for this dissociation, the vapour density agrees with the formula PCl_5. This formula also agrees with G. Oddo and E. Serra's determination of the mol. wt. from the effect of the pentachloride on the b.p. of carbon tetrachloride. Historically, phosphorus pentachloride played a part in the development of the concept of valency--*vide supra*, the valency of phosphorus—and in the idea of the so-called molecular compounds.

Phosphorus pentachloride is made by the action of an excess of chlorine on phosphorus, or by the action of dry chlorine on phosphorus trichloride. Moisture should be rigorously excluded so that the two components should be thoroughly dried. Since phosphorus pentachloride is a very unpleasant substance to manipulate in air, owing to the fact that it rapidly absorbs moisture, forming hydrochloric and phosphoric acids: $PCl_5 + 4H_2O = 5HCl + H_3PO_4$, H. Davy, E. Baudrimont, etc., found it best to make the compound in the bottle in which it was to be preserved. Fit the bottle with a three-hole stopper—one hole for the tube bringing in dry chlorine, one for the exit of the chlorine, and the third for a tap funnel by means of which phosphorus trichloride can be run into the chlorine drop by drop. Much heat is evolved during the reaction, so that it is well to keep the vessel well covered by a freezing mixture. H. A. Taylor described a modification of the process. W. Biltz and K. Jeep studied the thermal diagram of mixtures of phosphorus trichloride and chlorine, and the incomplete results, Fig. 49, are not incompatible with the assumption that a still higher polychloride exists. H. Müller obtained the pentachloride in crystals by passing chlorine into a soln. of phosphorus trichloride in carbon disulphide, when most of the pentachloride is precipitated as fast as it is formed. A. Michaelis made the compound by heating phosphorous chloride with sulphur monochloride: $3PCl_3+S_2Cl_2=PCl_5+2PSCl_3$, similarly with thionyl chloride; the presence of a trace of iodine acts as a stimulant on the reaction: $3PCl_3+SOCl_2=PCl_5+POCl_3+PSCl_3$, and an 88 per cent. yield can be obtained. H. Davy, and T. Thomson observed that the pentachloride is produced when chlorine is passed into phosphine; and R. Mahn obtained it by the action of phosphine on antimony pentachloride: $PH_3+4SbCl_5=4SbCl_3+3HCl+PCl_5$; and A. J. Balard, by the action of chlorine on the pentabromide. W. T. Casselmann said that phosphorus trichloride slowly decomposes on keeping, forming phosphorus and its pentachloride, but this observation needs verification. A. Michaelis and M. Pitsch obtained the pentachloride by the action of an excess of chlorine on phosphorus tetritoxide; A. Besson, on the hemioxide in the presence of carbon tetrachloride; T. E. Thorpe and A. E. H. Tutton, on phosphorous oxide; and H. Quantin, by heating ferric phosphate, or calcium phosphate, in the vapour of carbon tetrachloride. C. Poulenc heated phosphorus trifluodichloride to 200°–250°, and exposed it to the action of electric sparks: $5PF_3Cl_2=3PF_5+2PCl_5$.

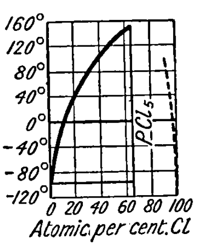


FIG. 49.—Thermal Diagram of the System: PCl_3–Cl_2.

Phosphorus pentachloride at ordinary temp. is a white, crystalline powder which fumes in air. According to P. Kremers, and A. Michaelis, it forms a mass of columnar crystals when cooled from the molten mass; and when obtained from a mixture of thionyl chloride, or, according to B. Corenwinder, by the action of chlorine on a sat. soln. of phosphorus in carbon disulphide, it appears in rhombic plates which, according to A. E. Nordenskjöld, belong to the tetragonal system, and have the axial ratio $a:c=1:0{\cdot}5672$. E. B. R. Prideaux found the sp. gr. of the solid at 160° to be 1·601, the sp. vol., 0·629; and the mol. vol., 128·9. The at. vol. of the contained phosphorus is 15·10. The thermal expansion represented by the vol., v, at $\theta°$, between 160° and 190° is $v=1+0{\cdot}00107\theta$. E. Mitscherlich[2] found the vap. density to be 4·85 (air unity) at 185°; and A. Cahours gave for the vap. densities at different temp.,

	182°	200°	230°	250°	274°	300°	327°	336°
Vap. density .	5·078	4·851	4·302	3·991	3·840	3·654	3·656	3·656
Dissociation .	41·7	48·5	67·4	80	87·5	96·2	97·3	97·3 per cent.

so that above 300°, the vap. density corresponds with 3·61, that of a mixture of equal vols. of phosphorus trichloride and chlorine. H. St. C. Deville noticed that the vapour has a yellowish-green colour at the higher temp This is due to the presence of free chlorine; the colour becomes darker the higher the temp. Paper moistened with starch and potassium iodide soln. also shows a blue coloration, characteristic of that produced by chlorine, when immersed in the vapour of phosphorus pentachloride at 157°–158°. A. Naumann calculated the percentage dissociation of the vapour, and his results are indicated above. A. Smith and R. H. Lombard obtained the following values for the vapour density:

	90°	100°	120°	140°	160°
Grains per c.c. .	$0{\cdot}0_3197$	$0{\cdot}0_3332$	$0{\cdot}0_3929$	$0{\cdot}0_22286$	$0{\cdot}0_24933$
Mols. per litre .	$0{\cdot}0_3945$	0·00159	0·00446	0·01096	0·02368

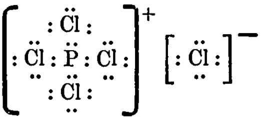
The vapour density at 90° is rather greater than the value required for the undissociated vapour; hence it is inferred that in the vicinity of 100°, some mols. of the vapour are associated into complexes. Above 110°, dissociation is evident. The dissociation of the pentachloride will be represented by the equation: $PCl_5 \rightleftharpoons PCl_3 + Cl_2$. If C_{PCl_5}, C_{PCl_3}, and C_{Cl_2} respectively denote the conc. of phosphorus pentachloride, phosphorus trichloride, and of chlorine, then, according to the mass law, for equilibrium: $kC_{PCl_5} = k'C_{PCl_3}C_{Cl_2}$. Suppose that 1 grm. of phosphorus pentachloride be heated in a closed vessel of vol. v. Let x represent the fraction dissociated at any given temp., then there will be C_{PCl_5}, or $(1-x)/v$ mols. of the pentachloride per unit vol.; C_{PCl_3}, or x/v mols. of the trichloride; and C_{Cl_2}, or x/v mols. of chlorine. Hence for equilibrium, the preceding equation reduces to $K = k/k' = x^2/(1-x)v$. It follows that by increasing the conc. of one of the products of the reaction, the dissociation of the pentachloride will be restrained. C. A. Wurtz confirmed this by showing that in the presence of an excess of the trichloride or chlorine the vap. density is near that required for the undissociated pentoxide. R. Wegscheider showed that in C. A. Wurtz's experiments the dissociation amounted to only 3–10 per cent. The reaction has been also studied by H. Wichelhaus, L. Troost and P. Hautefeuille, H. Debray, A. Horstmann, J. W. Gibbs, O. Brill, S. Dushman, R. Wegscheider, P. Blackman, C. Holland, and A. Smith and R. P. Calvert. A. Smith and R. H. Lombard gave for the dissociation press., p, of phosphorus pentachloride:

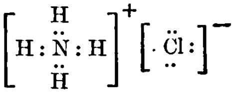
	90°	100°	110°	120°	130°	140°	150°	160°
p . . .	18	35	67	117	191	294	445	670 mm.

They represented the results by $\log p = -6724 \cdot 22T^{-1} - 19 \cdot 1978 \log T + 68 \cdot 9701$ for press. up to 160°. This result enables the mol. heat of vaporization to be calculated:

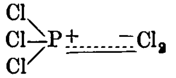
	90°	100°	110°	120°	140°	150°	160°
Heat of vaporization . .	14·2	15·6	16·6	16·9	15·6	14·9	14·9 Cals.

W. T. Casselmann[3] said that phosphorus pentachloride sublimes without melting when heated in air, but a very slight increase of press. suffices to melt it; volatilization occurs as low as 100°, and it sublimes rapidly at 160°. A. Naumann said that the b.p. is 160°–165°. E. B. R. Prideaux found that a thermometer placed in the vapour of phosphorus pentachloride subliming freely, and condensing on the bulb, remains steady at 160°. When the liquid pentachloride is slowly cooled, it begins to solidify at 162°. S. U. Pickering measured the lowering of the f.p. of benzene by phosphorus pentachloride. C. Feliciani found that the vapour of the pentachloride at 100 mm. press. has a thermal conductivity of 0·000165 at 148°, and 0·000234 at 291°. There are maxima, 0·00032 and 0·00033, respectively, at 230° and 270°, with a minimum of 0·000276 at 248°. M. Berthelot gave for the heat of formation (P,5Cl)=107·8 Cals.; J. Thomsen, (P,5Cl)=104·99 Cals., and $(PCl_3,2Cl)$=29·69 Cals. The heat of decomposition of phosphorus pentachloride by water was found by J. Thomsen to be 123·404 Cals.; J. J. B. Abria, 102·368 Cals.; T. Andrews, 109·504 Cals.; and P. A. Favre and J. T. Silbermann, 100·373 Cals. M. Berthelot and W. Longuinine found that one eq. of phosphorus pentachloride reacts with water evolving 118·9 Cals., and with a soln. of potassium hydroxide (1 : 50) evolving 220·1 Cals. The subject was discussed by H. W. Schröder van der Kolk, and J. Thomlinson. C. R. Crymble measured the absorption spectrum of the pentachloride. H. Davy, H. L. Buff, W. Hampe, and A. Voigt and W. Biltz said that this chloride is a non-conductor of electricity. Phosphorus pentachloride behaves like an electrolyte in a suitable solvent—*vide infra*, phosphorus pentabromide. A sat. soln. of phosphorus pentachloride in nitrobenzene was shown by G. W. F. Holroyd to be a conductor, and the introduction of phosphorus trichloride, and of hydrogen chloride reduced the conductivity; a soln. of the pentachloride in ethylene dibromide, benzene, or phosphorus trichloride passed no current. H. Henstock, and S. Sugden discussed the electronic structure; and in accord with the electrolytic character of the pentachloride, G. W. F. Holroyd represented the electronic structure, in a manner analogous to that of ammonium chloride:





According to T. M. Lowry, it is a general rule that if one atom shares two electrons with another, but contributes both electrons to the common stock instead of only one, it acquires a positive charge, whilst its neighbour (which has acquired a half-share in two electrons not originally belonging to it) becomes negatively charged. E. B. R. Prideaux added that regarding the PCl_5 mol. in this manner we see that the pair of chlorine atoms are both united to the phosphorus by a single duplet, and thus completely take the place of an oxygen or sulphur atom, and may be replaced by these but not by OH-groups. The fifth phosphorus valency is an electrovalency, but is not quite the same as an ordinary electrovalency: no electron has passed across and there is no ionization possible, except by passing into the tautomeric form of the NH_4Cl-type. That this mode of union may be a strong one is shown by the fact that PF_5 does not behave as a fluorinating agent. In the case of all halogen compounds which show that maximum valency of the element, halogen atoms equal in number to the hydrogen (or alkyl) valency in each case and replaceable by OH are united in a different manner from the remaining halogen atoms which are replaceable by oxygen or sulphur, or are left free in the lower valent compounds. This gives for phosphorus pentachloride:



explaining the easy detachment, by gaseous dissociation, of the two chlorine atoms.

The chemical properties of phosphorus pentachloride.—There are two important characteristics of the chemical reactions of phosphorus pentachloride: (i) The facility with which chlorine is given up by the scission of the molecule; this shows itself by its acting as an energetic chlorinating agent; and (ii) The tendency of phosphorus pentachloride to unite additively with other chlorides to form complex compounds. E. Baudrimont[4] found that a mixture of the pentachloride with **hydrogen** when passed through a red-hot tube, furnished some phosphorus, phosphine, hydrogen chloride, and phosphorus trichloride. H. Davy said that the pentachloride burns when placed in the flame of a candle; and when the vapour is mixed with **oxygen** and passed through a red-hot tube, phosphoric oxide and chlorine are formed, and, added E. Baudrimont, some phosphoryl chloride is produced at the same time. J. A. Wanklyn and A. Robinson found that the vapour at 300° begins to oxidize in **air.** According to H. Davy, phosphorus pentachloride reacts with **water,** forming phosphoric and hydrochloric acids: $PCl_5+4H_2O=H_3PO_4+5HCl$; but with steam, C. A. Wurtz observed the formation of phosphoryl chloride: $H_2O+PCl_5=POCl_3+2HCl$. G. Oddo assumed that when a mixture of phosphorus pentachloride with varying quantities of water is heated in a reflux apparatus, there is evidence of a step-by-step formation of the products: (i) $Cl_4P.O.PCl_4$; (ii) $Cl_3P{=}O_2{=}PCl_3$; (iii) $Cl_2P{\equiv}O_3{=}PCl_2$; (iv) $(PO_2Cl)_2$; and (v) P_2O_5. The first and penultimate products have not been isolated from the products of the reaction. With the mixture $2PCl_5+H_2O$, half of the pentachloride is converted into oxychloride, the rest being unchanged; the mixture $2PCl_5+2H_2O$ yields the theoretical amount of oxychloride; the mixture $2PCl_5+4H_2O$, or $(POCl_3)_2+H_2O$, gives mainly oxychloride accompanied by a little pyrophosphoryl chloride, $P_2O_3Cl_4$, and phosphoric oxide; and with the proportions $2PCl_5+4H_2O$, or $(POCl_3)_2+3H_2O$, the same products as in the previous case are obtained, the amount of oxychloride being considerably diminished, and that of phosphoric oxide correspondingly increased. M. Trautz observed no luminescence when phosphorus pentachloride reacts with cold or warm water.

H. Moissan found that when the pentachloride is treated with **fluorine,** the whole mass becomes incandescent, and the pentafluoride is formed; **chlorine** and **bromine** have no action; and W. Biltz and E. Meinecke observed that the pentachloride is insoluble in liquid chlorine; and K. H. Butler and D. McIntosh, that the pentachloride has no action on the b.p. of liquid chlorine. According to E. Baudrimont, **iodine** reduces a part of the pentachloride and forms an addition product, phosphorus iodohexachloride, $PCl_5.ICl$, thus: $3PCl_5+I_2=PCl_3+2PCl_5(ICl)$. G. Gore found that the pentachloride is vigorously decomposed by dry **hydrogen fluoride** at —18° to —29°, forming a white powder; and the pentachloride dissolves in liquid **hydrogen chloride,** forming a colourless soln. J. H. Gladstone said that when heated with **hydrogen bromide** there is no reaction; but with **hydrogen iodide,** C. A. Wurtz observed the formation of phosphorus trichloride, hydrogen chloride, and iodine. W. Spring said that when **chlorine trioxide** is passed over phosphorus pentachloride, there is often a vigorous explosion, chlorine monoxide being formed. R. Weber said that **iodic acid** decomposes the pentachloride at ordinary temp. H. Schiff observed that with **potassium chlorate,** phosphoryl chloride is formed.

J. H. Gladstone, and E. Baudrimont found that when phosphorus pentachloride and **sulphur** are fused together, thiophosphoryl chloride is formed. H. Goldschmidt obtained sulphur monochloride by the reaction: $2S+PCl_5=PCl_3+S_2Cl_2$; and O. Ruff found a soln. of phosphorus pentachloride in phosphoryl chloride reacts with sulphur in the presence of iodine forming sulphur monochloride. G. S. Sérullas, and E. Baudrimont represented the reaction with dry **hydrogen sulphide:** $PCl_5+H_2S=2HCl+PSCl_3$; while if a mixture of the two be passed through a red-hot tube, hydrogen chloride and phosphorus pentasulphide are formed. W. Biltz and H. Keunecke found that thiohydrolysis occurs when liquid hydrogen trisulphide is brought in contact with phosphorus pentachloride. H. Schiff represented the reaction which occurs when the pentachloride is warmed with dry **sulphur dioxide** by $PCl_5+SO_2=POCl_3+SOCl_2$; P. Kremers, and J. Persoz and N. Bloch seem to have thought that the product was a chemical individual—the former called it *schwefligsaures Phosphorchlorid,* and the latter *chlorophosphate biacidsulphurique.* A. Michaelis, and K. Heumann and P. Köchlin represented the reaction with dry **sulphur trioxide:** $PCl_5+2SO_3=S_2O_5Cl_2+POCl_3$; the reaction is slow, and requires the application of heat; if the phosphorus pentachloride is in excess, the pyrosulphuryl chloride is decomposed $S_2O_5Cl_2+PCl_5=POCl_3+2Cl_2+2SO_2$, and no thionyl chloride is formed. The reaction was examined by A. W. Williamson, and H. Schiff. A. Michaelis represented the reaction with conc. **sulphuric acid:** $3H_2SO_4+PCl_5=3SO_2(OH)Cl+HPO_3+2HCl$; and the chlorosulphonic acid reacts: $2SO_2(OH)Cl+PCl_5=S_2O_5Cl_2+2HCl+POCl_3$. S. Williams represented the reaction: $PCl_5+H_2SO_4=SO_2(OH)Cl+POCl_3+HCl$, and $2PCl_5+H_2SO_4=SO_2Cl_2+2POCl_3+2HCl$; but A. Michaelis said that no sulphuryl chloride is formed, and F. Baumstark, no phosphoryl chloride, and he represented the reaction with the fuming acid by $4H_2SO_4+PCl_5=4SO_2(OH)Cl+HCl+H_3PO_4$. S. Williams added that the phosphoryl chloride reacts with the sulphuric acid: $2H_2SO_4+POCl_3=2SO_2(OH)Cl+HPO_3+HCl$. The reaction with **chlorosulphonic acid** is indicated above, and with a smaller proportion of acid, A. Michaelis represented the reaction: $2SO_2(OH)Cl+PCl_5=S_2O_5Cl_2+2HCl+POCl_3$. He also found that **sulphuryl chloride** is slowly decomposed into thionyl and phosphoryl chlorides, and chlorine; H. E. Armstrong, and A. Michaelis, that **pyrosulphuryl chloride,** sulphur dioxide, phosphoryl chloride, and chlorine are formed, while A. Geuther represented the reaction: $S_2O_5Cl_2+PCl_5=2SO_2+2Cl_2+POCl_3$, and $PCl_5+SO_2=POCl_3+SOCl_2$. A. Michaelis and O. Schumann found that with **nitroxylsulphonic acid,** the reaction can be symbolized: $SO_2(NO_2)OH$

$+PCl_5=SO_2(OH)Cl+NOCl+POCl_3$. F. Ephraim and M. Gurewitsch found that **amidosulphonic acid** gives amidosulphuryl, phosphoryl, and hydrogen chlorides; and they also reported the formation of the complex $NH_2.SO_2Cl.PCl_3$—*phosphorus amidosulphuryltetrachloride.* W. Spring examined the action of the pentachloride on **thiosulphates**; and K. Kraut found that with thiosulphates it forms thionyl chloride. L. Carius said that **calcium sulphite** is decomposed by phosphorus pentachloride; and K. Kraut found that with **sodium thiosulphate,** thionyl chloride is formed. According to C. Pape, and J. Y. Buchanan, **lead thiosulphate** is decomposed when heated in the vapour of phosphorus pentachloride, and C. W. Blomstrand represented the reaction: $PbS_2O_3+2PCl_5=PbCl_2+POCl_3+PSCl_3+SO_2Cl_2$. E. Baudrimont found that when the pentachloride is heated with **selenium,** the reaction is: $PCl_5+2Se=PCl_3+Se_2Cl_2$. According to A. Michaelis, **selenium dioxide** reacts: $3SeO_2+3PCl_5=3SeOCl_2+3POCl_3$, and the products then interact: $3SeOCl_2+2POCl_3=3SeCl_4+P_2O_5$; E. Baudrimont said a yellow product is formed with **selenium monochloride** at ordinary temp., and this becomes red if heat be employed, but no selenophosphorus chloride is formed. R. Metzner obtained *tellurium phosphotridecachloride,* $2TeCl_4.PCl_5$, by heating **tellurium tetrachloride** and phosphorus pentachloride in a sealed tube at 220°. R. Weber found that **lead selenide** forms lead chloride and a red liquid which gives selenium and hydrogen selenide with water. E. Baudrimont reported that lead selenide at a red-heat forms lead chloride, phosphorus trichloride, and selenium tetrachloride, while **antimony triselenide** yields phosphorus and antimony trichlorides, and selenium monochloride.

H. Davy said that phosphorus pentachloride forms a definite compound with **ammonia**; and H. Rose observed that ammonia is slowly absorbed by the well-cooled pentachloride—*vide* phosphorus. The complex phosphorus chloronitrites, produced by the action of ammonia on the pentachloride, were examined by J. von Liebig and F. Wöhler, J. H. Gladstone, J. H. Gladstone and J. D. Holmes, A. Laurent, H. Wichelhaus, H. N. Stokes, J. Persoz, etc.—*vide* **8.** 49, 73. If ammonia be passed into a soln. of phosphorus pentachloride in carbon tetrachloride, A. Besson found that **phosphorus octamminopentachloride,** $PCl_5.8NH_3$, is formed as a white crystalline mass, which, at about 175°, decomposes into a chloronitrite. H. Perpérot found that when soln. of ammonia and of phosphorus pentachloride in carbon tetrachloride are mixed, impure **phosphorus decamminopentachloride,** $PCl_5.10NH_3$, is formed—*vide supra,* phosphorus trichloride. There is a break in the time-decomposition curve at 310° in agreement with that for ammonium chloride. Hence it is assumed that the decomposition product is a mixture of ammonium chloride and phosphorus pentamide. H. N. Stokes also found that the chloronitrites are produced by the action of the pentachloride on **ammonium chloride.** W. P. Winter observed that phosphorus pentachloride and **sodium amide** react vigorously when warmed, ammonium and sodium chlorides are sublimed, and a compound—possibly PO(NH)(OH) or OP≡NO—is formed. R. Müller found that the pentachloride reacts with **nitrogen peroxide,** forming nitrosyl and phosphoryl chlorides and chlorine. According to J. Persoz and N. Bloch, both **nitrous and nitric acids** react with the pentachloride, forming phosphoric acid, nitrogen, chlorine, and an oxygen compound; while H. Schiff obtained with nitric acid, hydrogen chloride, phosphoryl chloride, and a blood-red liquid. R. Weber decomposed **silver nitrate** by phosphorus pentachloride; and A. Naquet observed that with **potassium nitrate,** nitrosyl and phosphoryl chlorides are formed. J. H. Gladstone said that **phosphorus** has no appreciable action in the cold, but when heated it violently reduces the pentachloride to the trichloride. According to H. Rose, a small proportion of **phosphine** reacts: $3PCl_5+PH_3=3HCl+4PCl_3$; and with phosphine in excess, $3PCl_5+5PH_3=15HCl+8P$. The reaction was also studied by R. Mahn. T. E. Thorpe and A. E. H. Tutton observed that with **phosphorous oxide** there is a lively reaction, and phosphory and phosphorous chlorides are formed; M. Bakunin, and J. Persoz and N. Bloch, that **phosphoric oxide** yields phosphoryl chloride, but H. Schiff said that phosphorus pentoxide readily absorbs the vapours of the pentachloride, forming the complex $P_2O_5.2PCl_5$, or $P_4O_5Cl_{10}$, *phosphorus pentoxydecachloride.* This reaction was also examined by C. Gerhardt, and C. Gerhardt and L. Chiozza. A. Geuther found that the pentachloride reacts with **hypophosphorous acid:** $H_3PO_2+3PCl_5=2POCl_3+2PCl_3+3HCl$; and with **phosphorous acid:** $H_3PO_3+3PCl_5=PCl_3+3POCl_3+3HCl$. H. Schiff said that the pentachloride does not react with heated **metaphosphoric acid.** A. Geuther, however, represented the reaction: $HPO_3+2PCl_5=3POCl_3+HCl$; with pyrophosphoric acid, $H_4P_2O_7+5PCl_5=7POCl_3+4HCl$, or $H_4P_2O_7+PCl_5=2HPO_3+POCl_3+2HCl$; and with orthophosphoric acid, $H_3PO_4+3PCl_5=4POCl_3+3HCl$. H. Schiff said that the reaction **phosphoric acid** is very slow. R. Weber found that **sodium hydrophosphate** is decomposed by the vapour of phosphorus pentachloride. A. Geuther and A. Michaelis found a reaction with **pyrophosphoryl chloride:** $P_2O_3Cl_4+PCl_5=3POCl_3$. E. Baudrimont represented the reaction with **thiophosphoryl chloride:** $5PSCl_3+3PCl_5=3PBr_5+5PSCl_3$; and R. Weber, the reaction with **phosphorus pentasulphide,** $P_2S_5+3PCl_5=5PSCl_3$. E. Baudrimont, and H. Goldschmidt represented the reaction between powdered **arsenic** and the pentachloride by $4As+6PCl_5=4AsCl_3+6PCl_3$. M. Hurtzig and A. Geuther found that the reaction with **arsenic trioxide** results in the formation of arsenic trichloride, but no oxychloride, and with **arsenic pentoxide:** $As_2O_5+5PCl_5=2AsCl_3+2Cl_2+5POCl_3$—A. Michaelis said that arsenic pentoxide does not react with phosphorus pentachloride at 200°. T. E. Thorpe showed that with **arsenic trifluoride,** phosphorus pentafluoride is formed: $5AsF_3+3PCl_5=5AsCl_3+3PF_5$. A. W. Cronander said that **arsenic trichloride** reacts with the pentachloride, forming *arsenious phosphoctochloride,* $PCl_5.AsCl_3$, and *arsenic phosphodecachloride,* $AsCl_5.PCl_5$. E. Baudrimont found that the **arsenides** are decomposed when heated with phosphorus pentachloride; *realgar,* AsS, easily, but the following with difficulty: mispickel, FeAsS; *speiss cobalt,* $(Co,Ni,Fe)As_2$; *proustite,* Ag_3AsS_3; *pyrargyrite,* Ag_3SbS_3; *bournonite,* $CuPbSbS_3$; *fahlerz,* $(Cu_2,Ag_2,Fe,Zn)_3\{(As,Sb)S_3\}_2$; and *arsenical iron,* $FeAs_2$. E. Baudrimont said that powdered **antimony** reacts with the pentachloride more readily than does arsenic, forming antimony and phosphorus trichlorides. R. Mahn found that **stibine** produces phosphorus and antimony trichlorides, and hydrogen chloride. H. Schiff found that **antimony pentoxide** is not attacked when heated in contact with the pentachloride. E. Baudrimont observed that **antimony trichloride** forms a complex with phosphorus pentachloride, and R. Weber, and A. W. Cronander showed that both **antimony pentachloride** and trichloride form *antimony phosphodecachloride,* $SbCl_5.PCl_5$. T. Karantassis found that phosphorus pentachloride reacts with antimony triiodide liberating iodine and forming phosphorus trichloride, and the complex, $PCl_5.2SbCl_5$—*antimony phosphopentadecachloride*—$6PCl_5+2SbI_2=5PCl_3+2I_2+PCl_5.2SbCl_5$. E. Glatzel found **antimony trisulphide** is converted into this antimonyl sulphide.

H. Schiff observed that **potassium cyanide,** and **potassium ferrocyanide** are not decomposed by phosphorus pentachloride; but with **potassium thiocyanate,** a little sulphur monochloride, thiophosphoryl chloride, potassium chloride, sulphur, and phosphorus trichloride are formed. G. Gustavson found that some carbonyl chloride is produced when **sodium carbonate** is heated with the pentachloride. The use of phosphorus pentachloride for chlorinating **organic compounds** has been discussed by Lassar Cohn. It is in general use for replacing hydroxyl groups by chlorine, *e.g.* $(CH_2.COOH)_2+2PCl_5=(CH_2.CO.Cl)_2+2POCl_3+2HCl$; and with the acid anhydrides, $(CH_2CO)_2O+PCl_5=POCl_3+(CH_2.CO.Cl)_2$. The alcohols furnish the alkyl chlorides; and the amides their chlorine derivatives; the carbonyl oxygen of the aldehydes and ketones is replaced by Cl_2; chloral forms $CCl_3.CHCl_2$; etc. These reactions were investigated by G. F. Gerhardt, A. Cahours, A. Béchamp, M. Lies-Bodart, B. Rathke, E. Paterno, C. A. Wurtz, etc. C. T. Liebermann and L. Landshoff found that with ether the complex $(C_2H_5)_2O.3PCl_5$ is formed.

According to R. Mahn, **silane** slowly reduces phosphorus pentachloride to the trichloride. R. Weber said that **silica** is converted to silicon tetrachloride—the reaction with quartz is slow. R. Weber found that **titanium dioxide** yields a volatile chloride, and J. Tuttscheff showed that the complex *titanium phosphoenneachloride*, $TiCl_4.PCl_5$, is formed. S. R. Paijkul obtained *zirconium phosphotridecachloride*, $2ZrCl_4.PCl_5$, by the action of **zirconium tetrachloride** on phosphorus pentachloride in a sealed tube at 240°. According to G. Gustavson, when **boric oxide** is heated with the pentachloride for 3 or 4 days at 140°, boryl chloride is first formed, and later boron trichloride; J. Tarible found that with **boron tribromide,** a complex *boron phosphopentachlorohexabromide*, $2BBr_3.PCl_5$, is formed.

Phosphorus pentachloride transforms many **metals** into chlorides, and sometimes the excess unites with the metal chloride to form a complex—phosphorus trichloride is simultaneously formed. If the temp. is high enough, a metal phosphide may be formed. H. Davy found that if **potassium** is heated in the vapour of phosphorus pentachloride there is a lively combustion. A. C. Vournasos observed that the pentachloride reacts like the trichloride towards potassium. E. Baudrimont showed that cold **sodium** in contact with phosphorus pentachloride acquires a protective rind of sodium chloride. Molten sodium may inflame and detonate in contact with the pentachloride, forming phosphorus trichloride, but if the sodium is in excess, sodium phosphide is formed. According to H. Goldschmidt, **copper** reacts: $2Cu+PCl_5=2CuCl+PCl_3$, if an excess of the metal is present: $13Cu+2PCl_5=Cu_3P_2+10CuCl$; with **silver,** $2Ag+PCl_5=2AgCl+PCl_3$; and, according to E. Baudrimont, with **gold,** auric and phosphorous chlorides are formed. E. Baudrimont, W. T. Casselmann, and H. Goldschmidt found that with warm **zinc,** zinc and phosphorous chlorides are readily produced; but with the red-hot metal, zinc phosphide may be produced; E. Baudrimont found that **cadmium** behaves like zinc; and H. Goldschmidt represented the reaction with **mercury:** $Hg+PCl_5=HgCl_2+PCl_3$—*vide infra*, mercuric chloride. He also represented the reaction with **aluminium:** $2Al+3PCl_5=2AlCl_3+3PCl_3$. E. Baudrimont said that if the aluminium is red-hot, the phosphide may be produced as well; the aluminium chloride forms a complex with phosphorus pentachloride. The reaction was also studied by C. Matignon. E. Baudrimont found that **tin** forms stannous chloride which in turn forms a complex; with the pentachloride no phosphide was observed when the reaction occurs at a high temp. H. Goldschmidt symbolized the reaction: $Sn+2PCl_5=SnCl_4+2PCl_3$. E. Baudrimont said that with **iron** filings, ferrous, ferric, and phosphorous chlorides are formed, and the excess of the pentachloride forms a complex with ferric chloride. H. Goldschmidt represented the reaction: $Fe+PCl_5=FeCl_2+PCl_3$, and with the pentachloride in excess, ferric chloride is formed. M. M. Sobel said that phosphorus pentachloride fumes attacked every single metal tested up to 200°; but not so with **nickel,** and it has only a slight effect on **monel metal.** E. Fink found that with **palladium** and phosphorus pentachloride in a sealed tube, at 250°, a complex is formed. E. Baudrimont found that spongy **platinum** is easily converted into the tetrachloride which forms a complex with the excess of phosphorus pentachloride. P. Schützenberger thus obtained *platinous phosphoheptachloride*, $PtCl_2.PCl_5$. These reactions were studied by A. Rosenheim and co-workers. W. R. Hodgkinson and F. K. S. Lowndes showed that a platinum wire heated electrically in the vapour of phosphorus pentachloride forms a fusible platinum phosphide. G. Geisenheimer found that the pentachloride does not attack **iridium.** M. F. Schurigin, however, found both iridium and **ruthenium** are attacked at 300°, forming respectively *iridium triphosphododecachloride*, $IrCl_3.3PCl_3$, and *ruthenium pentaphosphoenneadecachloride*, $Ru_2(PCl_3)_5Cl_4$.

The **metal oxides** decompose at a red-heat in the vapour of phophorus pentachloride, forming the metal chloride and phosphoryl chloride. Thus, R. Weber observed that **magnesium oxide** so reacts with brilliant incandescence; **cadmium oxide** is likewise decomposed; and **aluminium oxide** produces a phosphochloride—

corundum and **spinel** are but slowly attacked. R. Weber found that **stannic oxide** forms stannic chloride. H. Schiff found that **chromic oxide** is converted into the violet chloride ; and **molybdenum trioxide** acts in the cold, forming white crystals of acid molybdenum chloride, and a sublimate of molybdenum trichloride, and, according to A. Piutti, the complex $MoCl_5.POCl_3$. E. F. Smith and G. W. Sargent heated molybdenum trioxide in the vapour of phosphorus pentachloride and chlorine, and obtained first phosphoryl chloride, and then the complex *molybdenum phosphodecachloride*, $MoCl_5.PCl_5$; no sign of molybdenum hexachloride was observed. A. W. Cronander found that **chromyl chloride** forms violet *chromic phosphooctochloride*, $CrCl_3.PCl_5$; and H. Schiff said violet chromic chloride and chlorine are the products of the reaction. J. Persoz and N. Bloch said that **tungsten trioxide** forms *tungsten trioxyphosphopentachloride*, $WO_3.PCl_5$; C. F. Gerhardt, C. H. Ehrenfeld, and H. Schiff and A. Piutti said that a sublimate of tungsten oxychloride is formed; and N. Teclu, that tungsten hexachloride and phosphoryl chloride are formed. A. W. Cronander found that **tungsten pentachloride** forms *tungsten phosphoenneachloride*, $WCl_4.PCl_5$; and with **uranium trioxide** in a sealed tube, yellow *uranium phosphodecachloride*, $UCl_5.PCl_5$, is formed. R. Weber found that **manganese oxide** is decomposed ; **ferric oxide** forms a complex ferric phosphochloride ; and that **titaniferous iron, chrome-ion,** and **franklinite** are decomposed.

H. Schiff said that **potassium chloride, bromide, or iodide** is not decomposed ; and A. W. Cronander added that the **alkali chlorides** do not form complex salts with phosphorus pentachloride. L. Pfaundler found that molten **silver fluoride** and the vapour of phosphorus pentachloride furnish phosphorus pentafluoride and silver chloride. L. Lindet found that with **auric chloride** the complex *auric phosphoenneachloride*, $AuCl_4.PCl_5$, is formed. E. Baudrimont prepared a complex with **mercuric chloride,** *mercuric phosphohexadecachloride*, $3HgCl_2.2PCl_5$, as a sublimate, by heating mercury or a chloride with phosphorus pentachloride. A. W. Cronander obtained the complex *molybdenum phosphodecachloride*, $MoCl_5.PCl_5$, when **molybdenyl chloride** is heated in the vapour of phosphorus pentachloride ; if the temp. is not so high, *molybdenum diphosphotetradecachloride*, $MoCl_4.2PCl_5$, is formed. He also obtained with **ferrous or ferric chloride** the complex *ferric diphosphoctochloride*, $FeCl_3.PCl_5$. According to R. Weber, and E. Baudrimont, the **metal sulphides** react with phosphorus pentachloride, forming thiophosphoryl chloride, the metal chloride, sulphur monochloride, and maybe a thiophosphate. E. Baudrimont found that **potassium sulphide** forms potassium chloride, thiophosphoryl chloride, and phosphorus pentasulphide ; analogous products are obtained with **calcium sulphide,** and **barium sulphide.** R. Weber found that **bismuth sulphide ; sphalerite,** ZnS ; **galena,** PbS ; and **marcasite,** FeS_2, are easily and completely decomposed. R. Weber found that **barytes** is decomposed when heated in the vapour of phosphorus pentachloride ; C. F. Gerhardt found that anhydrous **alum** furnishes a phosphate and hydrogen chloride, but no phosphoryl chloride. L. Carius observed that **lead sulphate** forms lead phosphate and sulphuryl chloride, while A. Michaelis obtained sulphur dioxide, chlorine, and phosphoryl chloride with a little thionyl and pyrosulphuryl chlorides, and a trace of sulphuryl chloride. J. Persoz and N. Bloch found that with **mercuric sulphate,** the complex *phosphorus sulphatodecachloride*, $SO_2.2PCl_5$, is formed. C. F. Gerhardt said that the products are phosphoryl, sulphuryl, and mercuric chlorides.

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§ 33. The Oxychlorides of Phosphorus

In 1847, C. A. Wurtz [1] obtained *phosphoryl chloride*, $POCl_3$, in his study of the action on phosphorus pentachloride, and since then a number of other oxychlorides have been reported—*e.g.* G. Gustavson's *metaphosphoryl chloridc*, PO_2Cl; A. Geuther and A. Michaelis' pyrophosphoryl chloride, $P_2O_3Cl_4$; and A. Besson's *phosphoryl monochloride*, POCl. In addition, G. N. Huntly showed that the reaction between phosphorus trichloride and phosphorus pentoxide at 200° is more complex than that represented by the simple equation: $POCl_3+P_2O_5=3PO_2Cl$, because pyrophosphoryl chloride is formed as well as another substance "which cannot have a simpler formula than $P_7O_{15}Cl_5$," and which "may prove to be a mixture." It might be added that a mixture or solid soln. $P_2O_5+5PO_2Cl$ has the required composition $P_7O_{15}Cl_5$.

The so-called **phosphoryl chloride,** $POCl_3$, or *phosphoryl trichloride*—when it is desired to distinguish it from the monochloride, POCl—or *phosphorus oxychloridc*, or *phosphoric oxychloride*, or *orthophosphoric chloride*, is formed in a great many reactions. Thus, it is produced during (i) *the oxidation of phosphorus trichloride* when heated in air (W. Odling [2]); and by the action of oxygen on the boiling trichloride (A. Michaelis). Other oxidizing agents may be used—*e.g.* ozone (I. Remsen); potassium chlorate (E. Dervin); sulphur trioxide (H. E. Armstrong, and A. Michaelis); selenium dioxide, thionyl chloride, or selenyl chloride (A. Michaelis); and nitrogen trioxide (A. Geuther and A. Michaelis). A. A. Vanscheidt and V. M. Tolstopiatoff made it by the simultaneous action of water and chlorine on phosphorus trichloride. This is affected by passing a stream of chlorine through phosphorus trichloride and adding, drop by drop, an equivalent quantity of water; the end of the reaction is recognized by the formation of phosphorus pentachloride and the yellow coloration of the liquid. The heat of the reaction maintains the liquid at the boiling point until the end; the boiling is then continued artificially for about half an hour. Phosphoryl chloride is produced during (ii) *the oxidation or hydrolysis* *of phosphorus pentachloride* when the vapour mixed with oxygen is heated to redness (E. Baudrimont); by the action of moist air or water in quantity insufficient to form orthophosphoric acid (C. A. Wurtz, and G. Oddo); by the action of acid hydrates (C. F. Gerhardt, and H. Schiff); sulphur dioxide (H. E. Armstrong); sulphur trioxide or the various sulphur oxychlorides (A. Michaelis); by potassium perchlorate, and by nitric acid (H. Schiff); by phosphorous oxide (T. E. Thorpe and A. E. H. Tutton); by phosphorus pentoxide (C. F. Gerhardt, H. Schiff and A. Piutti. J. Persoz and N. Bloch, and T. E. Thorpe); metaphosphoric acid (A. Geuther); pyrophosphoryl chloride (A. Geuther and A. Michaelis); by various metal oxides or oxygenated salts (L. Carius, A. Michaelis, J. Y. Buchanan, H. Schiff and A. Piutti, and N. Teclu); and by the action of oxygenated organic compounds (A. Cahours, and C. F. Gerhardt). (iii) The action of a small proportion of water or acetic acid on phosphorus trichlorodibromide was found by A. Geuther and A. Michaelis to yield phosphoryl chloride. Phosphoryl chloride is also produced (iv) *by the chlorination of phosphorus or the phosphorus oxides or hydrides*—thus, the action of chlorosulphonic acid on red phosphorus (K. Heumann and P. Köchlin); chlorine on phosphorus tetritoxide (A. Michaelis and M. Pitsch), phosphorus oxide (T. E. Thorpe and A. E. H. Tutton), or phosphoryl monochloride (A. Besson); sodium chloride (H. Kolbe and E. Lautemann) or carbon tetrachloride (G. Gustavson) on phosphoric oxide; chlorine on ethyl phosphate (H. Wichelhaus); and sulphuryl or thionyl chloride on phosphine (A. Besson). (v) *By the thermal decomposition of the oxychlorides*—*e.g.* by heating phosphoryl dichlorobromide, or pyrophosphoryl chloride.

C. F. Gerhardt prepared phosphoryl chloride by distilling phosphorus pentachloride with half its weight of thoroughly dried oxalic acid, or over one-fifth of its weight of boric acid. E. Dervin recommended oxidizing phosphorus trichloride with potassium chlorate: $KClO_3+3PCl_3=3POCl_3+KCl$. The reaction is somewhat violent; 500 grms. of pure phosphorus trichloride free from uncombined phosphorus are placed in a retort of 750–1000 c.c. capacity, connected with a reflux condenser, and 160 grms. of finely powdered potassium chlorate are added through the tubulure in quantities of about 4 grms. at a time, care being taken to wait each time until ebullition ceases before adding more chlorate. When the whole of the chlorate has been added, the liquid is distilled. The yield is very satisfactory, and the phosphoryl chloride contains but traces of chlorine. If too much chlorate be used, chlorine is produced: $2POCl_3+KClO_3=KCl+P_2O_5+3Cl_2$, and G. Oddo said that this usually occurs towards the end of the operation. F. Ullmann and A. Fornaro said that to avoid the formation of chlorine oxides, the chlorate should be quite dry; and to avoid risk of explosions, the chlorate should be covered with a little previously obtained phosphoryl chloride, and the phosphorus trichloride added gradually. A 95·6 per cent. yield can be obtained by this process.

According to J. Riban, when chlorine is passed over a mixture of normal calcium phosphate and carbon, or when chlorine and carbon monoxide are passed over normal calcium phosphate alone heated to incipient redness, small quantities of calcium chloride and metaphosphate are formed, but no further change takes place. If, however, a mixture of chlorine and carbon monoxide is passed over an intimate mixture of calcium phosphate and carbon (*e.g.*, bone-black), heated in a glass tube to 330°–340° in an oil-bath, phosphoryl chloride, calcium chloride, and carbon dioxide are produced. After some time, the calcium chloride formed interferes with the reaction, but if it is removed by washing, the phosphate can be completely decomposed. The carbon plays no chemical part in the reaction, and is found practically unaltered at the end of the experiment. It is, however, essential to the production of the reaction, and probably acts by condensing the gases in its pores. The reaction occurs in two stages, thus: $Ca_3P_2O_8+2CO+2Cl_2=CaP_2O_6+2CO_2+2CaCl_2$, and $CaP_2O_6+4CO+4Cl_2=2POCl_3+4CO_2+CaCl_2$. The reaction takes place slowly at 180°, and proceeds rapidly between 330° and 340°. Analogous processes were used by G. Erdmann, and A. Ogliagoro. E. I. du Pont de Nemours ct Cie. made it by the action of carbonyl chloride on a phosphate at say 300°–500°—

e.g. $FePO_4+3COCl_2=POCl_3+3CO_2+FeCl_3$. According to P. P. Budnikoff and E. A. Schiloff, for the reaction $\frac{1}{2}Ca(PO_3)_2+2CO+Cl_2\rightleftharpoons\frac{1}{2}CaCl_2+POCl_3+2CO_2+73{\cdot}8$ Cals., the equilibrium constant $K=p^2{}_{CO}p^2{}_{Cl_2}/p_{POCl_3}p^2{}_{CO_2}$; and $\log K=3{\cdot}8+1{\cdot}75T-16200T^{-1}$; and for the reaction: $\frac{1}{2}Ca(PO_3)_2+2COCl_2=2CO_2+POCl_3+\frac{1}{2}CaCl_2$, $K=p^2{}_{COCl_2}/p^2{}_{CO_2}p_{POCl_3}$, and $\log K=3{\cdot}4-1{\cdot}75\log T-5690T^{-1}$.

The physical properties of phosphoryl chloride.—Phosphoryl chloride is a clear, colourless, fuming liquid with a smell like that of phosphorus trichloride. C. A. Wurtz [3] gave 1·7 for the **specific gravity** of the liquid at 12°; H. Wichelhaus, 1·66; A. Cahours, 1·673 at 14°; D. I. Mendeléeff gave 1·662 at 19·5°; H. L. Buff, 1·6937 at 10°, 1·6887 at 14°–15°, 1·64945 at 51°, and 1·5091 at 110°; T. E. Thorpe, 1·71165–1·71185 at 0°, and 1·50967 at 107·23°—the b.p.; and T. E. Thorpe and A. E. H. Tutton, 1·71185–1·71190 at 0°. C. A. Wurtz found the **vapour density** to be 5·334 at 151°, 5·298 at 215°, and 5·295 at 275°. T. E. Thorpe obtained 1·13378 for the vol. of the liquid at the b.p. when the vol. at 0° is unity. For the **molecular volume** at the b.p., T. E. Thorpe obtained data between 101·37 and 101·57; E. B. R. Prideaux, 101·3; H. L. Buff, between 101·44 and 102·24; and E. Rabinowitsch, 100. O. Masson, S. Sugden, and J. A. Groshans studied the mol. vols. of the family of halides. According to W. Ramsay and J. Shields, the **surface tension** at 18° is 31·91 dynes per cm., and at 46·1°, 28·37 dynes per cm.; while the **specific cohesion** at 18° is $a^2=3{\cdot}88$ per sq. mm., and at 46·1°, 3·55 per sq. mm. The **surface energy** $\sigma(Mv)^{\frac{2}{3}}=647{\cdot}7$ ergs at 18°, and 588·0 ergs at 46·1°. N. von Kolossowsky studied the relation between the capillary constants and the heat of vaporization.

The **thermal expansion**, represented by the vol., v, at $\theta°$, when the vol. at 0° is unity, was found by T. E. Thorpe to be:

	0°	20°	40°	60°	80°	100°	107·23°
v . .	1·00000	1·02178	1·04471	1·06906	1·09507	1·12300	1·133615

and he represented the results by $v=1+0{\cdot}001064309\theta+0{\cdot}0000011266\theta^2+0{\cdot}0_8 5299\theta^3$. A. Geuther and A. Michaelis said that when the liquid is cooled to −10°, it can be solidified so as to furnish colourless, long, tabular or columnar crystals. The liquid is very liable to undercooling, but A. Besson found crystallization occurs when the surfused liquid is seeded with a crystal of phosphoryl chloride or chlorobromide. A. Geuther and A. Michaelis gave −1·5° for the **melting point**; A. Besson, +2°; and G. Oddo, +1·782°. The **boiling point** found by C. A. Wurtz, A. Cahours, H. L. Buff, and H. Wichelhaus approximated 110°; E. Dervin, and G. Oddo gave 107°–108°; T. E. Thorpe, 107·22°–107·23° at 760 mm.; P. Walden, 105·8° at 753 mm.; and F. Ullmann and A. Fornaro, 104·5°–105·5° at 783 mm. W. Ramsay and J. Shields gave 329° for the **critical temperature**; and D. A. Goldhammer, 331·8°. The effect of phosphoryl chloride on the b.p. and f.p. of a number of solvents has just been indicated. G. Oddo gave 69 for the f.p. constant; and 21·3 cals. for the **heat of fusion**; and P. Walden, 52·7 cals. for the **heat of vaporization.** The **heat of formation** found for the liquid by J. Thomsen is (P,O,3Cl)=146·0 Cals.; M. Berthelot and W. Louguinine gave 143·9 Cals., and M. Berthelot, 145·9 Cals. J. Thomsen also found for $(PCl_3,O)=70{\cdot}66$ Cals., and for the **heat of solution,** or decomposition by water, 72·19 Cals., and M. Berthelot and W. Louguinine found that one eq. of phosphoryl chloride develops 74·7 Cals. when mixed with water, and with a (1 : 50) soln. of potassium hydroxide, 148·7 Cals. J. C. Thomlinson made some inferences about the constitution from the thermochemical data.

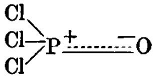
C. A. Wurtz found the liquid refracts light strongly. W. A. Miller examined the **absorption spectrum** of the liquid and showed that it completely absorbs the so-called chemical rays. H. L. Buff showed that the liquid is a non-conductor of electricity; while P. Walden found that at 105·0° and 753 mm. press. the sp. **electrical conductivity** is 0·0000022 mho, and is about equal to that of water of an average degree of purity. If the liquid has been in contact with moist air, the conductivity may rise 10 or 100 times this value. W. Finkelstein measured the **decomposition potential** of the oxychloride dissolved in bromine. H. Schlundt gave 13·9 for the **dielectric constant** at 22°.

Analyses of phosphoryl chloride by C. A. Wurtz,[4] J. H. Gladstone, A. Cahours, C. F. Gerhardt, T. E. Thorpe, G. Oddo, E. Dervin, and I. Remsen agree with the empirical formula $POCl_3$. The vapour density determinations of C. A. Wurtz, and A. Cahours are in agreement with the simple molecular formula $POCl_3$. W. Ramsay and J. Shields found no sign of the association of the molecules of the liquid when tested by the surface tension rule. The observations of G. Oddo and co-workers on the raising of the b.p. of soln. of phosphoryl chloride in carbon tetrachloride indicate that the molecule is more than doubled; while in benzene, and in carbon disulphide, there is a partial association of the simple molecules. The effect on the b.p. of chloroform, and ether agrees with the simple molecule. The mol. wt. for the doubled molecule is 307, and for the single molecule, 153·5. The means of the observed values are:

	CCl_4 (b.p.)	C_6H_6 (b.p.)	CS_2 (b.p.)	$CHCl_3$ (b.p.)	$(C_2H_5)_2O$ (b.p.)	C_6H_6 (f.p.)
Mol. wt.	332	298	232	161	152	151

E. Mameli found the effect of phosphoryl chloride on the f.p. of chloroacetic acid indicates a mol. wt. less than normal at low conc., and, increasing with conc., exceeds the normal value with a 1·3 per cent. conc.

There are two possible modifications of phosphoryl chloride, $Cl_2P.OCl$, and $Cl_3P : O$; in one, the phosphorus atom is tervalent, and in the other, quinquevalent —*vide supra*, the at. wt. of phosphorus. All attempts to isolate isomeric forms have failed. A. Michaelis and W. la Coste, however, did prepare derivatives of the two isomers, namely, phenoxydiphenylphosphine, $(C_6H_5)_2P.O.C_6H_5$, and phosphoryl triphenyl, $(C_6H_5)_3P : O$. The former is a thick, oily liquid which is readily acted upon by bromine, oxygen, sulphur, and selenium, and yields crystalline addition products with the alkyl halides; whereas the latter is a solid of m.p. 153·5°, and it resists the action of the agents just indicated. T. E. Thorpe and A. E. H. Tutton found that the phosphoryl chloride derived from phosphoric oxide is identical with that derived from phosphorous oxide. H. Wichelhaus thought that the constitution of phosphoryl chloride must be $Cl_2 : P.OCl$ because it is obtained by the action of chlorine on ethoxyphosphorus dichloride, $C_2H_5O.PCl_2$, in which it is highly probable that the oxygen is directly united with the phosphorus; the assumption is made that the reaction proceeds: $C_2H_5O.PCl_2+Cl_2 = C_2H_5Cl+ClO.PCl_2$, but A. Geuther and A. Michaelis have pointed out that it is possible the chlorine acts first by forming phosphorus trichloride: $C_2H_5O.PCl_2 + Cl_2 = C_2H_5OCl+PCl_3$; and the products of the reaction interact: $PCl_3+C_2H_5OCl = C_2H_5Cl+POCl_3$. T. E. Thorpe's conclusion that the sp. vol. of the contained phosphorus agrees with a tervalent phosphorus atom was shown by W. Ramsay and D. O. Masson to be ill-founded. The generally accepted formula $O : P : Cl_3$, based upon the quinquevalency of phosphorus, is not therefore inconsistent with H. Wichelhaus' reaction. It agrees with the formation of phosphoric acid when phosphoryl chloride is treated with water. It is also in agreement with B. Reinitzer and H. Goldschmidt's study of the action of phosphoryl chloride on the metals; no signs of any difference in the nature of the three chlorine atoms were observed; in all cases either none, or all three chlorine atoms were taken up by the metal. This agrees with the work of R. M. Caven, who progressively substituted the chlorine atoms in different ways with organic radicles and was not able to find any evidence justifying the assumption that the chlorine atoms are differently oriented within the molecule. He added: the centre of gravity of the three chlorine atoms lie at the angles of an equilateral triangle; and if an imaginary line is drawn through the centre of this triangle and at right angles to its plane, the centres of gravity both of the phosphorus atom and of the oxygen atom are situated in this line. E. B. R. Prideaux represents the electronic structure of phosphoryl chloride:



in which both electrons are contributed by the phosphorus atom, which has only half share in a pair originally belonging wholly to it, and is therefore positively charged—*vide supra*, phosphorus pentachloride—while the oxygen atom, having half a share in the same pair of electrons, to which it has not contributed, is negatively charged. A. E. Makovetzky made observations on the molecular structure; and H. Henstock, on the electronic structure.

The chemical properties of phosphoryl chloride.—H. P. Cady and R. Taft[5] studied a number of electrolytic reducing reactions with phosphorus oxychloride as a solvent, for soln. of potassium iodate, and ferric chloride are reduced although no hydrogen is present. C. A. Wurtz represented the action of **water** on phosphoryl chloride by the equation: $POCl_3+3H_2O=H_3PO_4+3HCl$. According to A. Besson, if a current of moist air is passed through phosphoryl chloride, a series of intermediate products of the oxidation to phosphoric acid are formed: (i) $2POCl_3+H_2O=2HCl+P_2O_3Cl_4$; (ii) $POCl_3+H_2O=2HCl+PO_2Cl$; and (iii) $POCl_3+3H_2O=3HCl+H_3PO_4$. G. Oddo also said that with one or two molecular parts of water, pyrophosphoryl chloride is formed along with some phosphoric acid, and that the proportion of the latter increases with that of the water. The speed of the reaction with water was measured by G. Carrara and I. Zoppellari as in the analogous case of phosphorus trichloride (*q.v.*); the velocity constant $k=0{\cdot}0000348$.

H. Schiff, and J. H. Gladstone observed no reaction between phosphoryl chloride and **chlorine, bromine,** or **iodine.** W. Biltz and E. Meinecke found that phosphoryl chloride is only slightly soluble in liquid chlorine. G. Oddo and M. Tealdi said that phosphoryl chloride dissolves **iodine monochloride.** A. Besson found that dry **hydrogen bromide** does not act at the b.p. of the chloride, and in a sealed tube, there is only a little action, but if the mixed vapours be passed through a tube at 400°–500°, the mixed and substitution products $POCl_2Br$, $POClBr_2$, $POBr_3$, and PBr_5 are said to be formed. He also found that **hydrogen iodide** dissolves in the liquid chloride and forms phosphorus triiodide and metaphosphoric acid—possibly also a little oxyiodide. H. Schiff found that phosphoryl chloride liberates iodine from **potassium iodide.** P. Walden also found that phosphoryl chloride dissolves the **alkali iodides,** forming yellow soln., also **manganese, cadmium, mercuric, and stannic iodides.** According to W. Spring, when the chloride is added to a cold soln. of **potassium chlorate,** a yellowish-green gas, possibly chlorine, is evolved; and G. Oddo represented the reaction: $KClO_3+2POCl_3=P_2O_5+3Cl_2+KCl$.

H. Prinz observed no reaction between phosphoryl chloride and **sulphur** when the mixture is heated in a sealed tube at 200° for a long time. C. A. Wurtz observed no reaction between **hydrogen sulphide** and the chloride when the mixture is exposed to sunlight; but A. Besson said that if a soln. of dry hydrogen sulphide in phosphoryl chloride be allowed to stand for some time, at 0°, there is a reaction: $2POCl_3+3H_2S=6HCl+P_2O_2S_3$; and at 100°, $2POCl_3+H_2S=2HCl+P_2O_2SCl_4$. G. Oddo and M. Tealdi found **sulphur monochloride and monobromide** dissolve in phosphoryl chloride. L. Carius represented the reaction with **calcium sulphite** at 150°, $2POCl_3+3CaSO_3=3SOCl_2+Ca_3(PO_4)_2$, but E. Divers said that no oxychloride of sulphur is formed when calcium, **sodium, or lead sulphite** reacts with phosphoryl chloride: $2POCl_3+6CaSO_3=3CaCl_2+Ca_3(PO_4)_2+6SO_2$. A. Michaelis represented the reaction at 160° with **sulphur trioxide:** $6SO_3+2POCl_3=P_2O_5+3S_2O_5Cl_2$; G. Oddo and A. Casalino studied the f.p. of the binary system: $POCl_3$–SO_3—*vide* sulphur trioxide; and S. Williams, and A. Michaelis, with **sulphuric acid:** $2H_2SO_4+POCl_3=2SO_2(OH)Cl+HPO_3+HCl$. L. Carius represented the reaction with **sulphates:** $3PbSO_4+2POCl_3=3SO_2Cl_2+Pb_3(PO_4)_2$, but A. Michaelis could not verify this. K. Kraut observed no reaction with **thiosulphates.** A. Besson observed no reaction in the cold with **hydrogen selenide,** but, at 110°, $4POCl_3+5H_2Se=10HCl+P_2Se_5+2PO_2Cl$. A. Michaelis observed that with **selenyl chloride,** phosphorus pentoxide and selenium tetrachloride are formed. V. Lenher found that when warmed with **tellurium dioxide,** tellurium tetrachloride is formed; and with an excess of phosphoryl chloride, the complex *tellurium phosphorylheptachloride,* $TeCl_4.POCl_3$.

C. A. Wurtz found that a white solid is produced when **ammonia** reacts with phosphoryl chloride; and H. Schiff represented the reaction: $POCl_3+6NH_3=PO(NH_2)_3+3NH_4Cl$. J. H. Gladstone found that at 0°, *phosphoryl dichloroamide,* $PO(NH_2)Cl_2$, is formed by a reaction which may be symbolized: $POCl_3+2NH_3=POCl_2(NH_2)+NH_4Cl$; and at ordinary temp. there is a slow formation of phosphoryl chlorodiamide, $PO(NH_2)_2Cl$, by the reaction: $POCl_3+4NH_3=POCl(NH_2)_2+2NH_4Cl$—this change is rapid at 100°. When these substitution products are heated, they decompose $POCl_2(NH_2)=2HCl+N\equiv PO$; and $POCl(NH_2)_2=NH_4Cl+N\equiv PO$. H. Perpérot mixed soln. of phosphoryl chloride and of ammonia in carbon tetrachloride, and obtained impure **phosphoryl hexamminotrichloride,** $POCl_3.6NH_3$—*vide supra,* phosphorus trichloride. If phosphoryl chloride be sat. with ammonia, or mixed with **ammonium chloride,** heated to 100°–220°, and the product treated with water, diamido- and triamido-pyrophosphoric acids are formed (*q.v.*). F. E. Brown and J. E. Snyder found that phosphoryl chloride and **vanadium oxytrichloride** are miscible in all proportions, but almost immediately a reaction sets in, and a brown precipitate forms. A. Mente also studied these reactions, and with **ammonium carbonate** he observed no formation of phosphoryl triamide. E. J. Mills found that phosphoryl chloride reacts with **nitrates,** forming the corresponding metal chloride, phosphorus pentoxide, etc. H. Schiff, and J. H. Gladstone observed no reaction with **phosphorus,** but at 200°–250° in a sealed tube, B. Reinitzer and H. Goldschmidt said that there is a vigorous reaction resulting in the formation of phosphorus tetritoxide (*q.v.*): $4P+POCl_3=P_4O+PCl_3$. H. Schiff, and J. H. Gladstone said that phosphoryl chloride does not react with **phosphine;** and A. Besson said that there is no reaction with cold **phosphonium bromide,** but in a sealed tube at 150°, phosphorus hemioxide is formed (*q.v.*); and with **phosphonium iodide,** phosphorus diiodide and metaphosphoryl chloride are formed. G. Oddo and M. Tealdi observed that **phosphorus trichloride and pentachloride** as well as **phosphorus tribromide and pentabromide** dissolve in this menstruum. G. Gustavson heated equimolar proportions of phosphoryl chloride and **phosphorus pentoxide** to 200° in a sealed tube for 36 hrs., and represented the resulting formation of metaphosphoryl chloride: $P_2O_5+POCl_3=3PO_2Cl$. A. Geuther said that phosphoryl chloride does not react with **phosphoric acid** in the cold, but when heated with a large proportion of the chloride metaphosphoric acid is formed: $2H_3PO_4+POCl_3=3HPO_3+3HCl$; and with a small proportion of the chloride, pyrophosphoric acid is produced: $5H_3PO_4+POCl_3=3H_4P_2O_7+3HCl$; the reaction with **pyrophosphoric acid** is very slow: $2H_4P_2O_7+POCl_3=5HPO_3+3HCl$; with **phosphorous acid:** $2H_3PO_3+3POCl_3=3HPO_3+2PCl_3+3HCl$; and with **hypophosphorous acid:** $6H_3PO_2+3POCl_3=3HPO_3+2H_3PO_3+4P+9HCl$. H. Schiff observed no reaction with **silver phosphate.** L. Carius obtained thiophosphoryl chloride and phosphorus pentoxide by heating to 150° a mixture of **phosphorus pentasulphide** and phosphoryl chloride. B. Reinitzer and H. Goldschmidt found that with **arsenic** at 250°, phosphorus and arsenic trichlorides, phosphorus pentoxide, and pyrophosphoryl chloride are formed. A. Michaelis observed no reaction with **arsenic trioxide** at 160°. G. Oddo and M. Tealdi observed that phosphoryl chloride dissolves **arsenic fluoride, chloride, and bromide;** and P. Walden, **arsenic triiodide,** and **antimony triiodide.** R. Weber obtained the complex *antimony phosphoryloctochloride,* $SbCl_5.POCl_3$, with **antimony pentachloride** and phosphoryl chloride; G. Oddo and M. Tealdi also obtained this compound;

and they found that **bismuth chloride and bromide** dissolve phosphoryl chloride.

J. Riban found that the vapour of phosphoryl chloride is decomposed by red-hot **carbon,** forming phosphorus trichloride. H. Schiff observed no reaction with **carbon dioxide ;** and H. Hübner and G. Wehrhane, none with **silver cyanide** at 180°. P. Walden found that numerous organic compounds dissolve in phosphoryl chloride ; and G. Oddo and M. Tealdi, that **carbon tetrachloride** dissolves in that menstruum. S. Cloez, and A. Geuther and F. Brockhoff found that the reaction between phosphoryl chloride and **sodium ethoxide** results in the formation of ethyl phosphate : $3C_2H_5ONa+POCl_3=3NaCl+PO(OC_2H_5)_3$. D. Balareff said that when the calculated quantity of **alcohol** is added drop by drop to phosphoryl chloride cooled in a freezing mixture, hydrogen chloride, and methyl or ethyl chloride are evolved when the mixture is warmed, and *alkyl metaphosphate* remains : $POCl_3+2C_2H_5OH =2HCl+POCl(OC_2H_5)_2$; and $POCl(OC_2H_5)_2=C_2H_5Cl+C_2H_5PO_3$. M. Riegel studied the action on **phenol.** As shown by A. Béchamp, H. Ritter, C. F. Gerhardt, H. Schiff, and I. I. Kanonnikoff, phosphoryl chloride is used for preparing chloro-derivatives of alcohol: $3C_2H_5OH+POCl_3=3C_2H_5Cl+H_3PO_4$; and with **sodium acetate :** $2CH_3COONa+POCl_3=NaCl+NaPO_3+2CH_3COCl$, but not from acetic acid alone. A. Béchamp and C. St. Pierre found that with silver acetate: $3CH_3COOAg+2POCl_3=3CH_3COCl+3AgCl+P_2O_5$. The use of phosphoryl chloride in organic chemistry was discussed by Lassar Cohn. G. Oddo and M. Tealdi found that phosphoryl chloride dissolves **silicon tetrachloride and tetrabromide.** A. Wehrlin and E. Giraud, and R. Weber prepared titanium phosphorylheptachloride, $TiCl_4.POCl_3$; and O. Ruff and R. Ipsen, *titanium diphosphoryldecachloride,* $TiCl_4.2POCl_3$, by the action of **titanium tetrachloride** on phosphoryl chloride. G. Gustavson found that with **boric oxide** and phosphoryl chloride in a sealed tube there is formed a complex *boron phosphorylhexachloride :* $B_2O_3+2POCl_3 =PBO_4+BCl_3.POCl_3$; and the same complex is formed by the action of **boron trichloride** on phosphoryl chloride. G. Oddo and M. Tealdi obtained *boron phosphoryl tribromotrichloride,* $BBr_3.POCl_3$, with **boron tribromide ;** and H. Moissan found that **boron triiodide** reacts vigorously with this chloride.

J. H. Gladstone observed no reaction between phosphoryl chloride and **potassium** at ordinary temp., and B. Reinitzer and H. Goldschmidt also observed no reaction with the alkali metals at 100°, but at 180°, in a sealed tube, the reaction is explosively violent. Finely divided **copper** reacts between 150° and 200°: $39Cu+10POCl_3=30CuCl+3Cu_3P_2+2P_2O_5$; and $P_2O_5+4POCl_3=3P_2O_3Cl_4$; with **silver** at 250°, $2Ag+POCl_3=Ag_2O+PCl_3$; $3Ag_2O+POCl_3=Ag_3PO_4+3AgCl$, or $5Ag_2O+2POCl_3=Ag_4P_2O_7+6AgCl$; $Ag_3PO_4+POCl_3=P_2O_5+3AgCl$; and $P_2O_5 +4POCl_3=3P_2O_3Cl_4$. At ordinary temp., **magnesium** reacts very slowly with phosphoryl chloride ; the reaction is energetic at 100°, and phosphorus trichloride, magnesium chloride and phosphide, and a red substance, possibly the suboxide, are formed ; **zinc** also reacts slowly at ordinary temp., and rapidly at 100°, $9Zn+4POCl_3=6ZnCl_2+3ZnO+P_4O$; and $4ZnO+2POCl_3=Zn(PO_3)_2+3ZnCl_2$; the reaction was also examined by W. T. Casselmann. G. Denigès said that if a good pinch of zinc powder is placed in a test-tube and one or two drops of phosphoryl chloride are added (the zinc must be in excess), there is frequently an instantaneous production of flame ; in all cases, on the addition of a little water, minute flames of hydrogen phosphide appear. With the trichloride, this reaction is not produced. According to B. Reinitzer and H. Goldschmidt, phosphoryl chloride and an excess of **mercury** at 290° react, forming mercuric chloride, a red phosphide, phosphorus trichloride, pyrophosphoryl chloride, and a trace of phosphorus pentoxide. At 100°, **aluminium** furnishes phosphorus trichloride, aluminium chloride and phosphate, and a red substance—possibly the suboxide. Only slight signs of a reaction were observed with **lead** at 250°, but **tin** reacts at 100°. At 100°–120°, **iron** filings react: $Fe+POCl_3=FeO+PCl_3$; $6FeO+2POCl_3 =3FeCl_2+Fe_3(PO_4)_2$; and $2POCl_3+Fe_3(PO_4)_2=3FeCl_2+2P_2O_5$.

According to H. Bassett and H. S. Taylor, **cuprous or cupric oxide** furnishes the chloride as the main product when in contact with phosphoryl chloride either at ordinary temp. or at 100°. On the other hand, when freshly ignited **calcium oxide** and phosphoryl chloride are mixed and allowed to stand at the ordinary temp., or gently boiled, a complex *calcium oxybisphosphoryltrichloride*, $CaO.2POCl_3$, is formed; while under different conditions *calcium oxytrisphosphoryltrichloride*, $CaO.3POCl_3$, may be produced; M. Garino and M. Raffaghello observed the formation of the complex *calcium dihydroxybisphosphoryltrichloride*, $Ca(OH)_2.2POCl_3$, with **calcium hydroxide.** There were also formed complexes $Ca(OH)_2.2POCl_2.2C_2H_5(NH_2)$, and $Ca(OH)_2.2POCl_2.2(C_2H_5)_2O$. Similarly, **magnesium hydroxide** forms *magnesium dihydroxybisphosphoryltrichloride*, $Mg(OH)_2.2POCl_3$. H. Bassett and H. S. Taylor found that **magnesium oxide** in a sealed tube at 110° forms either *magnesium oxybisphosphoryltrichloride*, $MgO.2POCl_3$, or *magnesium oxytrisphosphoryltrichloride*, $MgO.3POCl_3$; similarly, **zinc oxide** furnishes *zinc oxytrisphosphoryltrichloride*, $ZnO.3POCl_3$; **cadmium oxide** reacts at ordinary temp. or at 100°, forming cadmium chloride as the chief product; likewise also **mercuric oxide,** and alumina. On the other hand, **manganese oxide** furnishes *manganese oxytrisphosphoryltrichloride*, $MnO.3POCl_3$; while **ferric oxide,** and **cobaltous oxide** yield the metal chloride as in the case of copper, cadmium, mercury, and aluminium oxides. If the reactions occur in the presence of organic solvents—acetone, methyl benzoate, or ethyl acetate—complex pyrophosphoryl compounds are formed. M. Garino and M. Raffaghello obtained with **nickelous hydroxide** an impure complex, *nickelous dihydroxybisphosphoryltrichloride*, $Ni(OH)_2.2POCl_3$.

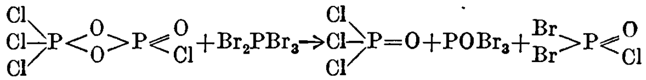
P. Walden found that phosphoryl chloride dissolves **auric chloride** in the cold. W. T. Casselmann found that phosphoryl chloride unites readily with many **metal chlorides,** thus, with **magnesium chloride** it forms magnesium phosphorylheptachloride, $2MgCl_2.POCl_3$; with **aluminium chloride** it forms *aluminium phosphorylhexachloride*, $AlCl_3.POCl_3$. G. Oddo and M. Tealdi obtained both these compounds. E. P. Köhler obtained with **aluminium bromide,** *aluminium phosphoryltribromotrichloride*, $AlBr_3.POCl_3$; H. Moissan obtained with **zinc fluoride,** zinc chloride and phosphoryl fluoride; and analogous products were obtained by A. Guntz with **lead fluoride**; while W. T. Casselmann obtained with **stannous chloride** the complex *stannous phosphorylheptachloride*, $2SnCl_2.POCl_3$; and also a complex with **stannic chloride,** $SnCl_4.POCl_3$, *stannic phosphorylheptachloride*, while G. Oddo and M. Tealdi represent as *stannic phosphorylhenachloride*, $2SnCl_4.POCl_3$. W. T. Casselmann obtained with **chromyl chloride** the products chromic oxide and chloride, and phosphoric acid. A. Piutti reported *molybdenum phosphorylhexachloride*, $MoCl_3.POCl_3$, to be formed by the action of **molybdenum trichloride** and phosphoryl chloride in a sealed tube at 170°. P. Walden, and G. Oddo found that sublimed **ferric chloride** forms a yellowish-brown soln. with phosphoryl chloride; and G. Oddo, that **platinic chloride** is dissolved by the menstruum.

A. Besson[6] prepared **phosphoryl monochloride,** POCl, by the action of a small quantity of water—whether liquid, or as atm. moisture—on phosphorus trichloride. The compound is isolated by distilling off the trichloride, at first on a water-bath and finally under low press. This oxychloride is a yellowish, hyaline solid of the consistency of paraffin, with an odour recalling that of the ordinary phosphoryl chloride. It is very hygroscopic, and dissolves in water with a strident noise, the products being hydrochloric acid, phosphorous acid, and a small quantity of an amorphous yellow solid. It is rapidly decomposed by light with formation of a pale yellow precipitate which changes to reddish-yellow if the action of light is prolonged. The oxychloride is insoluble in most solvents, but dissolves in phosphorous trichloride. It combines slowly with chlorine, and yields phosphoryl chloride, $POCl_3$. The yield of phosphorous oxychloride is always very small, probably because its formation is limited by its extremely hygroscopic nature.

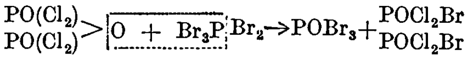
A. Geuther and A. Michaelis[7] prepared **pyrophosphoryl chloride,** $P_2O_3Cl_4$, by the action of nitrogen trioxide or peroxide on well-cooled phosphorus trichloride—

the trichloride yields about one-tenth its weight of the pyrophosphoryl chloride. B. Reinitzer and H. Goldschmidt obtained it as a by-product of the action of copper, silver, mercury, phosphorus or arsenic on phosphoryl chloride; and G. N. Huntly, by the action of phosphorus pentoxide on phosphoryl chloride—the product $P_7O_{15}Cl_5$ was obtained at the same time, *vide supra*. A. Besson said that in the preparation of phosphorus hemioxide (*q.v.*) by the action of phosphonium bromide on phosphoryl chloride, when the filtrate is heated in vacuo, pyrophosphoryl chloride distilled off after the phosphoryl chloride—metaphosphoryl chloride remains as a residue. A. Besson also found that pyrophosphoryl chloride is formed by the action of a current of moist air on phosphoryl chloride, $2POCl_3+H_2O=2HCl+P_2O_3Cl_4$—some phosphoric acid and metaphosphoryl chloride are formed at the same time. He also heated 300 grms. of phosphoryl chloride and 30 grms. of water first on a water-bath, and then in a sealed tube at 100°. When the product is heated in vacuo, pyrophosphoryl and phosphoryl chlorides distil over, and metaphosphoryl chloride and phosphoric acid remain behind. When the distillate is heated in vacuo at 25°–30°, the phosphoryl chloride distils off, and about 5 grms. of pyrophosphoryl chloride remain. G. Oddo also prepared this chloride by heating a mixture of 2 mols of phosphorus pentachloride and 3 mols of water under 3 cms. press. between 125° and 127°.

Pyrophosphoryl chloride was analyzed by A. Geuther and A. Michaelis, G. Oddo, and G. N. Huntly, and the results are in accord with the empirical formula $P_2O_3Cl_4$. If pyrophosphoryl chloride has the symmetrical formula $Cl_2 : PO.O.PO : Cl_2$, the rupture of the molecule in the reaction $P_2O_3Cl_4=POCl_3+PO_2Cl$ must be attended by the transfer of a chlorine atom from one part to the other, and D. Balareff supposes that the unsymmetrical formula for the pyrophosphoryl chloride, $Cl_3 : P<O_2>PO.Cl$, best explains this reaction. The symmetrical and the unsymmetrical formulæ explain equally well the reaction with phosphorus pentachloride: $P_2O_3Cl_4+PCl_5=3POCl_3$, but with phosphorus pentabromide, the reaction is somewhat curious; with the unsymmetrical formula it is represented:



and with the symmetrical formula:



$$\begin{matrix}PO(Cl_2)\\PO(Cl_2)\end{matrix}>\boxed{O\ +\ Br_3P}Br_2\rightarrow POBr_3+\begin{matrix}POCl_2Br\\POCl_2Br\end{matrix}$$

A. Geuther and A. Michaelis consider this to be the strongest argument in favour of the symmetrical formula, but D. Balareff argues that the reaction is here so complex that it has not yet been made out whether $POCl_2Br$ alone is formed or whether phosphoryl chloride, $POCl_3$, is produced along with phosphoryl bromide, $POBr_3$. D. Balareff also considers that the chemical properties of pyrophosphoryl chloride agree very well with the unsymmetrical formula for the chloride, and the chemical properties of pyrophosphoric acid with the unsymmetrical formula $(HO)PO<O_2>P(OH)_3$.

Pyrophosphoryl chloride is a colourless, fuming liquid which remains liquid at temp. where phosphoryl chloride is solid. A. Besson did not solidify the liquid at —50°. A. Geuther and A. Michaelis gave 1·58 for the sp. gr. at 7°, and 210°–215° for the b.p. It cannot be distilled without some decomposition: $3P_2O_3Cl_4=4POCl_3+P_2O_5$; and A. Besson said that at 110° and 10 mm. press., the compound decomposes: $P_2O_3Cl_4=POCl_3+PO_2Cl$. A. Geuther and A. Michaelis said that water decomposes it faster than it does phosphoryl chloride, forming hydrochloric and phosphoric acids; alcohol reacts: $2P_2O_3Cl_4+4C_2H_5OH=4PO(OC_2H_5)Cl_2+2H_2O$, followed by $PO(OC_2H_5)Cl_2+2H_2O=PO(OC_2H_5)(OH)_2+2HCl$; phosphorus pentachloride reacts: $P_2O_3Cl_4+PCl_5=3POCl_3$; and phosphorus pentabromide: $P_2O_3Cl_4+PBr_5=2POBrCl_2+POBr_3$. M. Riegel studied its action on phenol.

H. Bassett and H. S. Taylor found that when lime is added to a soln. of phosphoryl chloride in acetone, ethyl acetate, methyl benzoate, or ethyl benzoate, which had been dried over calcium chloride and redistilled, a vigorous reaction occurred which in the first two cases was sufficient to cause the solvent to boil. Some hydrogen chloride is evolved during this process, and the lime passes into soln. The soln. on cooling deposits prismatic crystals of **calcium oxypyrophosphoryl chloride,** $CaO.P_2O_3Cl_4$, associated with two mols of the solvent ketone or ester: $CaO,P_2O_3Cl_4,2C_3H_6O$; $CaO,P_2O_3Cl_4,2C_4H_8O_2$; $CaOP_2O_3Cl_4,2C_8H_8O_2$; and $CaO,P_2O_3Cl_4,2C_9H_{10}O_2$. In agreement with this view is the fact that the organic part of the molecule can be changed by simple recrystallization from another solvent. Thus, by recrystallizing the ethyl acetate compound from acetone, the acetone compound is obtained, and *vice versa.* Similar compounds of the organic ester or ketone associated with **copper oxypyrophosphorylchloride,** $CuO.P_2O_3Cl_4$; **magnesium oxypyrophosphorylchloride,** $MgO.P_2O_3Cl_4$; **cadmium oxypyrophosphorylchloride,** $CdO.P_2O_3Cl_4$; and **manganese oxypyrophosphorylchloride,** $MnOP_2O_3Cl_4$, can be prepared. The formation of these organic compounds is brought about by traces of moisture present in the organic solvents, or which are absorbed during the course of the experiment, and there is some reason for thinking that the moisture acts preferably on the previously formed compound $CaO,2POCl_3$, rather than on the phosphoryl chloride. In any case, the organic compounds can be obtained equally well by treating the previously prepared compound, $CaO,2POCl_3$, with the organic solvent in which it dissolves, yielding a soln. from which the organic derivative of the compound $CaO,P_2O_3Cl_4$ crystallizes. The zinc and cobaltous compounds could not be obtained in a crystalline form.

G. Gustavson[8] prepared **metaphosphoryl chloride,** PO_2Cl, by heating eq. quantities of phosphorus pentoxide, and phosphoryl chloride in a sealed tube at 200° for 36 hrs.: $P_2O_5+POCl_3=3PO_2Cl$. G. N. Huntly could not obtain this substance in this way—he always obtained a mixture of pyrophosphoryl chloride and $P_7O_{15}O_5$, indicated above. T. E. Thorpe and A. E. H. Tutton obtained it by passing a current of chlorine not too quickly over phosphorous oxide: $P_4O_6+4Cl_2=2POCl_3+2PO_2Cl$. The phosphoryl chloride can be distilled from the metaphosphoryl chloride—10 grms. of phosphorous oxide yield about 14 grms. of phosphoryl chloride and 9 grms. of metaphosphoryl chloride. A. Besson observed that metaphosphoryl chloride is formed during the action of hydrogen selenide on phosphoryl chloride: $4POCl_3+5H_2Se=10HCl+P_2Se_5+2PO_2Cl$; as a by-product in the action of phosphonium bromide on phosphoryl chloride in the preparation of phosphorus hemioxide—*vide supra,* pyrophosphoryl chloride; by the action of moist air on phosphoryl chloride—*vide supra,* pyrophosphoryl chloride; and by heating pyrophosphoryl chloride at 110° and 10 mm. press.—*vide supra.* The syrupy mass was found by A. Besson to decompose when heated: $3PO_2Cl=POCl_3+P_2O_5$.

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§ 34. The Phosphorus Bromides and Oxybromides

The observations of A. J. Balard,[1] H. Rose, A. Schrötter, and V. Merz and W. Weith on the union of bromine and phosphorus have been indicated in connection with phosphorus itself. W. Müller-Erzbach said that phosphorus has a smaller affinity for bromine than it has for chlorine. There are two well-defined bromides, analogous to the tri- and penta-chlorides; a heptabromide has been reported. A. Besson and L. Fournier attempted to prepare *phosphorus dibromide*, PBr_2, or P_2Br_4, analogous to the corresponding chloride and iodide, by the action of the silent discharge on a mixture of phosphorus tribromide and hydrogen, and by the action of hydrobromic acid on phosphorus dichloride, but without success. A reddish-yellow solid of indefinite composition was obtained, and this is supposed to be a decomposition product of the dibromide.

The formation and preparation of phosphorus tribromide.—A. J. Balard first prepared **phosphorus tribomide**, PBr_3, by very slowly adding bromine, drop by drop, to dry phosphorus. C. Löwig added small pieces of phosphorus to anhydrous bromine until the liquid is colourless, and the tribromide was distilled from the excess of phosphorus. A. Lieben said that if the phosphorus, etc., is well-cooled by a freezing mixture there is no risk of explosion. In order to avoid the risk of an explosion, H. Rose recommended introducing dry phosphorus into a glass tube sealed at the bottom and placed upright in liquid bromine contained in a wide-mouthed bottle, so that the bromine vapour may slowly come in contact with the phosphorus. The tribromide is also produced by slowly adding bromine to red phosphorus, and distilling the product; J. Volhard moderated the reaction by first moistening the phosphorus with phosphorus tribromide. R. Schenck, and A. C. Christomanos said that when an excess of phosphorus is employed the product is always contaminated with phosphatic products which cannot be removed by many rectifications; and R. Schenck preferred to use an excess of bromine which is more easily removed by fractional distillation. F. A. Kekulé dissolved 239·88 parts of bromine, and 31 parts of phosphorus separately in carbon disulphide; slowly mixed the products; and separated the solvent from the tribromide by distillation. This method was employed by J. Volhard, V. Rekschinsky, and G. Oddo and M. Tealdi, while A. C. Christomanos added that the solvent is not a suitable one since it is difficult to obtain pure, and it is liable to yield a product contaminated with sulphur compounds. A. C. Christomanos said that an 88 per cent. yield of tribromide of a high degree of purity can be obtained if bromine be allowed to act on yellow phosphorus, free from arsenic, under a layer of benzene free from thiophene. A. Lieben prepared the tribromide by passing the vapour of bromine in a current of carbon dioxide over dry phosphorus; allowing the product to stand for a day in contact with phosphorus; and distilling the decanted liquid. No considerable rise of temp. occurs so long as the bromine vapour is in contact with phosphorus. J. I. Pierre employed this process, but A. C. Christomanos added that the operation consumes a lot of time, the yield is poor, there is a loss of bromine, and the product is contaminated with other phosphatic products. C. Löwig passed the vapour of phosphorus over mercurous or mercuric bromide heated in a glass tube, and collected the product in a cooled receiver. The liquid was rectified by fractional distillation. He also observed the formation of a little tribromide by the action of phosphorus on warmed cyanogen bromide; A. Besson, by the action of hydrogen bromide on phosphorus trichloride; and E. Baudrimont, by passing carbon dioxide over phosphorus pentabromide heated in a flask on a water-bath.

The physical properties of phosphorus tribromide.—Phosphorus tribromide is a clear, mobile, fuming liquid with a smell recalling that of hydrogen bromide. A. C. Christomanos said that usually the liquid becomes faintly turbid on standing for some time on account of the separation of phosphorus held in soln. The soln. clears again if warmed up to near the b.p. The liquid colours the skin orange-yellow, and paper dark yellow or black, especially if warmed. J. I. Pierre gave 2·9249 for the sp. gr. of the liquid at 0°; T. E. Thorpe, 2·92311 at 0°, and 2·49541 at 172·9°, the b.p.; G. Carrara and I. Zoppelari, 2·9132 at 11°/4°; and A. C. Christomanos, 2·88467 at 0°, 2·85234 at 15°, and 2·82053 at 27°. O. Masson, S. Sugden, and J. A. Groshans studied the mol. vols. of the family of halides; and F. Ephraim calculated that a 10·8 per cent. expansion occurs during the formation of the tribromide. F. M. Jäger found for the sp. gr. referred to water at 4°, the surface tension, σ, in dynes per cm., the specific cohesion, a^2, per sq. mm., and the mol. surface energy, μ, in ergs per cm. in nitrogen gas:

	−20°	0°	20·8°	50·3°	75·7°	99·8°	154°	170°
Sp. gr. .	2·972	2·923	2·871	2·799	2·735	2·676	2·542	2·502
a^2 . .	3·14	3·12	3·05	3·01	2·90	2·74	2·28	2·14
σ . .	45·8	44·7	43·2	41·3	38·9	36·0	28·4	26·3
μ . .	927·0	916·8	894·7	870·0	832·1	781·4	637·9	597·0

R. Lorenz and W. Herz studied the relations between the surface tensions of the family of halides. H. Kopp gave for the mol. vol. at the b.p., 108·6; E. B. R. Prideaux, 108·8; T. E. Thorpe, 108·28; and E. Rabinowitsch, 111. The vap. density found by A. C. Christomanos was 135·44 for hydrogen unity, at 182°; and for air unity, 9·3589. This in conjunction with C. Löwig's analysis is in agreement with the formula PBr_3. G. Oddo and M. Tealdi found that the mol. wt. obtained from the effect on the f.p. of phosphoryl chloride is 271; and benzene, 261·8—the theoretical value for PBr_3 is 271. T. E. Thorpe, and J. I. Pierre observed that the thermal expansion is "extremely regular"; T. E. Thorpe gave for the vol. at different temp. when the vol. at 0° is unity:

	0°	40°	60°	80°	100°	120°	140°	172·9° (b.p.)
Vol. .	1·0000	1·0348	1·0530	1·0720	1·0961	1·1123	1·1340	1·17140

and he represented his results for the vol., v, at $\theta°$ by $v=1+0{\cdot}0_3841170\theta+0{\cdot}0_6542892\theta^2+0{\cdot}0_818893\theta^3$; and J. I. Pierre found for temp. between 0° and 100°, $v=1+0{\cdot}0_3847200\theta+0{\cdot}0_643672\theta^2+0{\cdot}0_82528\theta^3$; and between 100° and 175°, $v=1+0{\cdot}0_3824270\theta+0{\cdot}0_6914210\theta^2+0{\cdot}0_{10}55\theta^3$. D. I. Mendeléeff, and P. de Heen made observations on this subject. A. C. Christomanos found the coeff. of cubical expansion to be 0·0007554 at 15°, and 0·0007876 at 27°, so that the effect is greater than is the case with mercury. 1. I. Saslowsky studied the relation between the coeff. of expansion and the mol. structure; and N. de Kolossowsky, the relation between the coeff. of expansion and the latent heat of vaporization. A. J. Balard did not freeze the liquid at —12°, nor did J. I. Pierre at —13·6°; but A. C. Christomanos gave —41·5° for the f.p. at 761 mm. press. F. M. Jäger gave —50° for the f.p., and —40° for the m.p. J. I. Pierre gave 175·3° for the b.p. at 760·2 mm.; F. A. Kekulé, and H. Kopp, 175°; T. E. Thorpe, 172·9°; F. M. Jäger, 170·2° at 750 mm.; P. Walden, 172° and 757 mm.; G. Oddo and M. Tealdi, 170°; and A. C. Christomanos, 170·8° at 760 mm. and 171° at 761 mm. C. M. Guldberg calculated the critical temp. to be 441°. M. Berthelot gave for the heat of formation, $(P,3Br_{liq.})=PBr_{3liq.}+42·6$ Cals.; and M. Berthelot and W. Longuinine, $(P,3Br_{gas})=PBr_{3liq.}+54·6$ Cals., while one eq. of the tribromide in reacting with water yields 64·1 Cals., and with a (1 : 50) soln. of potassium hydroxide, 130·5 Cals. A. C. Christomanos found the index of refraction to be 1·6945 at 19·5° with Na-light. P. Walden said that phosphorus tribromide is a non-conductor of electricity, and does not ionize dissolved salts and acids; he also measured its conductivity in liquid sulphur dioxide and arsenic trichloride. H. Schlundt obtained 3·88 for the dielectric constant at 20°.

The chemical properties of phosphorus tribromide.—A. Besson and L. Fournier said that when a mixture of **hydrogen** and the vapour of phosphorus tribromide is exposed to the silent discharge, there is formed an unstable dibromide —*vide supra.* According to J. H. Gladstone, phosphorus tribromide is not attacked by **oxygen**; and A. C. Christomanos also found that oxygen has no appreciable action on the cold liquid, but E. Demole showed that if oxygen be passed through the boiling liquid, an explosion occurs after a certain time with the liberation of bromine, etc. He represented the reaction: $2PBr_3+O_2=2POBr+2Br_2$; $POBr+Br_2=POBr_3$; and $PBr_3+Br_2=PBr_5$; while A. C. Christomanos attributed the reaction to the liberation of bromine, and the combustion of the phosphorus with a yellowish flame of "blinding brilliance": $2PBr_3+5O=P_2O_5+3Br_2$. He also said that the tribromide is non-combustible, and does not ignite at ordinary temp., nor does the vapour from the boiling liquid inflame, though it does burn with a yellowish flame when in the vicinity of another flame—phosphorus pentoxide and bromine are formed. A. J. Balard, and C. Löwig said that in the presence of moisture, phosphorus tribromide reddens blue litmus; and A. J. Balard, and A. C. Christomanos found that the tribromide reacts with **water,** forming phosphorous and hydrobromic acids, and, if only a little water is employed, hydrogen bromide is evolved as a gas. The reaction, added C. Löwig, is slow at 8°, but very rapid at 35°. G. Carrara and I. Zoppelari found the velocity constant of the heterogeneous reaction to be 0·0111 at 5°, and 0·0212 at 10°.

A. J. Balard, and J. H. Gladstone found that the tribromide reacts with **chlorine**: $2PBr_3+3Cl_2=2PCl_3+3Br_2$; and, according to C. Löwig, it reacts with **bromine,** forming the pentabromide (*q.v.*). J. H. Gladstone, and A. C. Christomanos found that **iodine** dissolves in the liquid tribromide without reacting chemically. The liquid is cherry-red. A. Damoiseau observed that the tribromide is decomposed by conc. aq. soln. of **hydrobromic acid.** E. Baudrimont showed that thiophosphoryl bromide is formed when phosphorus tribromide is heated in contact with sulphur. U. Antony and G. Magri found that the tribromide dissolves in liquid **hydrogen sulphide,** forming a yellow, conducting soln. J. H. Gladstone represented the reaction with hydrogen sulphide: $2PBr_3+3H_2S=P_2S_3+6HBr$. G. N. Guam and J. A. Wilkinson observed that the soln. in liquid hydrogen sulphide is an electrical conductor.

H. Rose said that the tribromide behaves like the trichloride when treated with **ammonia**; and liquid ammonia, according to C. Hugot, reacts with the tribromide, forming phosphorus triamide (*q.v.*). A. Besson found that dry ammonia acts on a soln. of phosphorus tribromide in carbon tetrachloride, forming *phosphorus enneaamminotribromide,* $PBr_3.9NH_3$. A. Geuther and A. Michaelis observed that **nitrogen peroxide, and trioxide** react with the tribromide, forming phosphorus pentoxide and phosphoryl bromide. C. Löwig, R. Schenck, and A. C. Christomanos observed that the tribromide dissolves **phosphorus** which separates out when the soln. is decomposed by water—*vide supra,* red phosphorus. K. Kraut said that the tribromide reacts with **phosphorous acid** like the trichloride, but at a somewhat higher temp. P. de Wilde said that **phosphine** reacts quickly with the tribromide, forming hydrogen diphosphide (*q.v.*), and, added A. Besson, the reaction occurs even at —20°. A. Michaelis found that **thiophosphoryl bromide** dissolves in the liquid; and P. Walden, that the **trihalides of arsenic and antimony** are readily soluble in the cold liquid tribromide.

J. Tarible found that with **boron tribromide** much heat is developed and *boron phosphohexabromide*, $PBr_3.BBr_3$, is formed. A. C. Christomanos said that the liquid is very corrosive towards organic matter—leather, wood, paper, cork, rubber, etc.; he also found that phosphorus tribromide dissolves in **carbon disulphide, ether, acetone, chloroform,** and **benzene,** forming clear soln. without developing heat. When the ethereal soln. is evaporated, much hydrobromic acid is formed. P. Walden also showed that many **organic compounds** are soluble in the liquid bromide—*e.g.* hydrocarbons, acids, ketones, esters, tertiary amines, etc. A. C. Christomanos found that absolute **alcohol** reacts turbulently with the tribromide, without inflammation, forming traces of esters or phosphines. J. W. Walker and F. M. G. Johnson studied the action of methyl, ethyl, and *n*-propyl alcohols on phosphorus tribromide. The reactions are typified by $PBr_3+3CH_3OH=2CH_3Br+HBr+P(OH)_2(OCH_3)$. V. Auger found that phosphorus tribromide reacts with **methyl, ethyl, or propyl iodide** to form alkyl phosphines. A. C. Christomanos studied the action of the tribromide on **glycerol,** and **phenol.** R. Schenck found that **glass** is strongly attacked by the tribromide at an elevated temp.

A. C. Christomanos found that a small piece of **sodium** floats on the cold or warm liquid losing its metallic lustre; but if a little hot or cold water be sprinkled on the surface, there is a violent explosion; **sodium-amalgam** under similar conditions gives burning hydrogen; and **magnesium** acts like sodium, but the reaction is less violent and there is no explosion. A. Granger obtained copper phosphide by heating the tribromide with **copper** in a sealed tube; and when **iron, nickel, or cobalt** is heated in the vapour of the tribromide, the metal phosphide is formed. A. C. Christomanos found that **copper nitrate,** solid or in soln., reacts vigorously with the tribromide, and cuprous bromide, bromine, and nitrogen peroxide are formed; L. Lindet observed that when heated with **aurous bromide,** *aurous phosphotetrabromide*, $AuBr.PBr_3$, is formed. J. H. Gladstone observed an interchange of the halogens when phosphorus tribromide reacts with **mercuric chloride**; and H. Moissan represented the reaction with **zinc fluoride**: $3ZnF_2+2PBr_3=2PF_3+3ZnBr_2$; a similar reaction occurs with lead fluoride, but it proceeds more slowly. P. Walden found that the **stannic halides** dissolve in the cold liquid tribromide, and that with the iodide, the soln. is yellow. H. S. Fry and J. L. Donnelly found that phosphorus tribromide reacts like the trichloride towards **chromyl chloride.** G. Geisenheimer observed the complex *iridium triphosphododecabromide*, $IrBr_3.3PBr_3$; and M. F. Schurigen, *iridium phosphohexabromide*, $IrBr_3.PBr_3$, when the tribromide is heated with **iridium** in a sealed tube at 300°; and **ruthenium** under similar conditions yields *ruthenium pentaphosphoenneadecabromide*, $Ru_2(PBr_3)_5Br_4$.

H. Rose observed that phosphine forms a brownish-yellow precipitate with a soln. of mercuric bromide; and P. Lemoult observed that by the action of phosphine on a soln. of mercuric bromide in one of potassium bromide, a brown compound is formed, **phosphorus bromomercuriate,** $P(HgBr)_3.PHg_2Br$.

The formation and preparation of phosphorus pentabromide.—A. J. Balard first obtained **phosphorus pentabromide,** PBr_5, as a sublimate when an excess of bromine acts on phosphorus; and A. J. Balard, and C. Löwig obtained it by mixing theoretical proportions of phosphorus tribromide and bromine. W. Biltz and K. Jeep studied the thermal diagram of mixtures of phosphorus tribromide and bromine, Fig. 50, and obtained evidence of the existence of three polybromides, **phosphorus heptabromide,** $PBr_5.Br_2$; **phosphorus enneabromide,** $PBr_5.2Br_2$; and **phosphorus heptadecabromide,** $PBr_5.6Br_2$. The pentabromide can be obtained by metathetical reactions; thus, J. H. Gladstone found that liquid bromine sinks in liquid phosphorus trichloride without reacting, but if a little iodine is added, much heat is developed by the reaction: $2PCl_3+I_2+5Br_2=2PBr_5+2ICl_3$; H. Moissan showed that when phosphorus trifluoride is passed into bromine cooled to −15°, brown liquid phosphorus dibromotrifluoride is formed; this gradually decomposes: $5PF_3Br_2=3PF_5+2PBr_5$, the pentabromide remains in the tube, the pentafluoride escapes as a gas. A. Michaelis obtained it by the action of phosphorus pentachloride on thiophosphoryl bromide: $5PSBr_3+3PCl_5=5PSCl_3+3PBr_5$; A. Besson, by passing a mixture of the vapours of phosphoryl chloride and hydrogen bromide through a glass tube at 400°–500°; E. Demole. by the action of oxygen on boiling phosphorus tribromide—*vide supra;* and T. E. Thorpe and A. E. H. Tutton, by the action of bromine on phosphorous oxide in a sealed tube at ordinary temp.

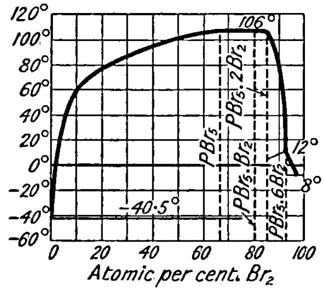

FIG. 50.—Thermal Diagram of the System: PBr_3–Br_2.

The properties of phosphorus pentabromide.—Phosphorus pentabromide at ordinary temp. is a lemon-yellow solid which A. J. Balard described as appearing in rhombohedral crystals after melting, and in needle-like crystals after sublimation. According to A. E. Nordenskjöld, the rhombic bipyramids have the axial ratios $a:b:c=0·6032:1:0·4010$. E. Baudrimont said that the crystals are red when the molten pentabromide is cooled slowly, and yellow, if cooled rapidly. H. Moissan made analogous observations. Consequently, it has been maintained that the yellow rhombic and the red prismatic varieties are allotropic forms of the pentabromide; but J. H. Kastle and W. A. Beatty explained the difference on the assumption that the red form is phosphorus heptabromide—*vide infra*—and the yellow form the pentabromide. The former in contact with water produces white phosphoryl bromide, and the latter passes into soln. without forming this product. E. B. R. Prideaux found the sp. and mol. vols. of liquid phosphorus pentabromide at 85° to be respectively 0·3530 and 152·1; at 100°, 0·3621 and 156·0; at 130°, 0·3755 and 161·7; and at 165°, 0·3899 and 168·0. The at. vol. of the contained phosphorus is greater with the bromide than with the chloride; and greater with tervalent than with quinquevalent phosphorus. There is a point of inflexion in the expansion curve at 100° corresponding with that of sulphur at 159°. The expansion from 85° to 100° is represented by $v=v_{85}(1+0·0019\theta)$, and from 100° to 165° by $v=v_{100}(1+0·0012\theta)$. Analyses by C. Löwig, H. Moissan, and T. E. Thorpe and A. E. H. Tutton agree with the formula PBr_5, and G. Oddo and M. Tealdi's observation on the lowering of the f.p. of phosphoryl chloride, and of benzene by the dissolved pentabromide agree with the simple mol. PBr_5. According to A. J. Balard, when the pentabromide is heated, it melts to a red liquid which, at a higher temp. gives off red vapours, and, added J. H. Gladstone, a mixture of phosphorus tribromide and bromine is formed at 100°, and the pentabromide is reformed on cooling. E. Baudrimont said that if carbon dioxide be passed into a bulb containing the pentabromide heated by a water-bath, bromine passes off and the tribromide remains. J. H. Kastle and W. A. Beatty said that the dissociation of the pentabromide dissolved in carbon disulphide or tetrachloride soon attains a limiting value. E. B. R. Prideaux gave 106° for the estimated b.p. at 760 mm. The observed vap. press., p mm., being:

	23°	41°	61°	75°	79°	88°	100°	106°
p . .	6	35	109	217	237	337	560	(760)

According to J. Ogier, the heat of formation of the solid pentabromide is $(P,5Br_{liq.})=63·5$ Cals.; $(P,5Br_{gas})=83·0$ Cals.; $(P,5Br_{solid})=63·3$ Cals.;

($PBr_3, Br_{2liq.}$)=20·3 Cals. P. Walden examined the electric conductivity of the pentabromide dissolved in liquid sulphur dioxide or arsenic trichloride. W. A. Plotnikoff observed that phosphorus pentabromide dissolved in bromine conducts an electric current, depositing phosphorus on the cathode, and combines with bromine to form pentabromide. W. Finkelstein measured the decomposition potential of the pentabromide in bromine, liquid sulphur dioxide, arsenic trichloride, and nitrobenzene.

A. J. Balard said that the pentabromide is not reduced by **hydrogen,** it fumes strongly in **air,** and deliquesces in humid air, forming, according to J. H. Gladstone, phosphoryl bromide. A. J. Balard recognized that the pentabromide is decomposed by **water,** forming phosphoric and hydrobromic acids. M. Trautz observed no signs of luminescence when hot or cold water reacts with phosphorus pentabromide. A. J. Balard showed that the pentabromide is decomposed by **chlorine,** forming bromine and phosphorus trichloride. W. Finkelstein observed that when soln. of phosphorus pentabromide in **bromine** are electrolyzed, the phosphorus moves towards the cathode. J. H. Gladstone showed that **iodine** reacts: $3PBr_5+I_2=3PBr_3+2IBr_3$. E. Baudrimont found that with **hydrogen sulphide** thiophosphoryl bromide is formed: $PBr_5+H_2S=PSBr_3+2HBr$; and F. Clausnitzer, that conc. **sulphuric acid** forms hydrogen bromide, bromine, sulphur dioxide, and sulphur bromide. A. Besson found that dry **ammonia** passed into a soln. of the pentabromide in carbon tetrachloride furnishes *phosphorus enneaamminotetrabromide*, $PBr_5.9NH_3$; and J. H. Gladstone, that with **phosphine** the first stage of the reaction is to be symbolized: $3PBr_5+PH_3=4PBr_3+3HBr$, and then $PBr_3+PH_3=2P+3HBr$. E. Berger observed that **phosphorus pentoxide** forms phosphoryl bromide. A. Michaelis found that **thiopyrophosphoryl bromide** is converted into thiophosphoryl bromide; and A. Geuther and A. Michaelis, that **pyrophosphoryl chloride** reacts: $P_2O_3Cl_4+PBr_5=2POCl_2Br+POBr_3$. E. Baudrimont found that **antimony trisulphide** reacts: $Sb_2S_3+3PBr_5=3PSBr_3+2SbBr_3$. G. Gustavson showed that **boric oxide** reacts with phosphorus pentabromide with difficulty, forming boron tribromide. J. Tarible added that a soln. of **boron tribromide** in carbon disulphide furnishes crystals of *boron phosphoctobromide*, $BBr_3.PBr_5$. The pentabromide reacts with **acetic acid**: $PBr_5+CH_3COOH=POBr_3+HBr+CH_3COBr$; and E. Baudrimont, with **oxalic acid**: $PBr_5+(COOH)_2=POBr_3+2HBr+CO+CO_2$. A. J. Balard observed that when heated in contact with the **metals,** phosphorus pentabromide usually forms the metal phosphide and bromide; with **gold,** L. Lindet obtained *auric phosphoctobromide*, $AuBr_3.PBr_3$. A. Rosenheim and W. Levy said that **platinum** reacts at 170°–200°, forming *platinous phosphopentabromide*, $PtBr_2.PBr_3$. M. F. Schurigen found that in a sealed tube at 310° **iridium** and **ruthenium** are attacked by phosphorus pentabromide, forming respectively *iridium phosphohexabromide*, $IrBr_3.PBr_3$, and *ruthenium pentaphosphoenneadecabromide*, $Ru_2(PBr_3)_5Br_4$. C. Löwig observed that **copper and mercury oxides** form bromides and phosphate; and E. Baudrimont with **lead oxide,** the reaction is attended by a glow of the mass.

Phosphorus heptabromide, PBr_7, was prepared by J. H. Kastle and W. A. Beatty by mixing equimolar proportions of bromine and phosphorus pentabromide in a sealed tube, and subliming at 90°. The product occurs as bright red, transparent crystals. The red form of phosphorus pentabromide is considered to be the heptabromide. Its formation by subliming the yellow pentabromide at 90° is said to be due to a partial decomposition into heptabromide and tribromide; phosphorus tribromide reconverts it into the yellow pentabromide. Bromine vapour converts the yellow pentabromide into the red compound, whilst when left in contact with bromine absorbents the reverse change takes place. In contact with water, phosphorus pentabromide gives a colourless soln. of phosphoric and hydrobromic acids, whilst the red compound liberates free bromine.

J. H. Gladstone found that when phosphorus pentabromide is oxidized by exposure to air it deliquesces, forming a red syrupy liquid of **phosphoryl bromide,**

$POBr_3$, or *phosphorus oxybromide ;* E. Berger oxidized the pentabromide by the pentoxide : $P_2O_5+3PBr_5=5POBr_3$; and, as indicated above, H. Ritter obtained it by the reaction of acetic acid on the pentabromide ; and E. Baudrimont, by the action of oxalic acid. A. Geuther and A. Michaelis also obtained it by the action of pyrophosphoryl chloride on the pentabromide : $PBr_5+P_2O_3Cl_4=POBr_3+2POBrCl_2$; and by treating phosphorus dibromotrichloride with water : $3PCl_3Br_2+3H_2O=2POCl_3+POBr_3+3HCl+3HBr$; or with acetic acid : $2PCl_3Br_2+3CH_3COOH=3CH_3COCl+POBr_3+POCl_3+HBr+H_2O$. Phosphoryl bromide is also produced by oxidizing phosphorus tribromide—*e.g.*, E. Demole, by the action of oxygen on the boiling tribromide ; and A. Geuther and A. Michaelis, by the action of nitrogen peroxide or trioxide on the well-cooled tribromide. A. Besson observed that phosphoryl bromide is produced when a mixture of the vapour of phosphoryl chloride and hydrogen bromide is passed through a tube at 400°–500°, and by the action of a soln. of bromine in carbon tetrachloride on phosphorus hemioxide. T. E. Thorpe and A. E. H. Tutton noted its formation by the action of bromine on phosphorous oxide : $P_4O_6+4Br_2=2POBr_3+2PO_2Br$.

E. Baudrimont described phosphoryl bromide as an orange mass consisting of thin, colourless plates ; H. Ritter also said that the crystals are colourless plates, with sp. gr. 2·822. Analyses by J. H. Gladstone, H. Ritter, and E. Baudrimont agree with the formula $POBr_3$; and the values of the vapour density 10·06, obtained by J. H. Gladstone, and 10·11, obtained by E. Berger, are close to 9·94 required for $POBr_3$. G. Oddo and co-workers found the mol. wt., calculated from the effect on the b.p. of chloroform, to be 298 ; on the b.p. of benzene, 344 ; and on the f.p. of benzene, 300. The value for $POBr_3$ is 287. H. Ritter gave for the m.p. 45°–46° ; E. Baudrimont, 35° ; A. Besson, 56° ; E. Berger, 55°–56° ; and T. E. Thorpe and A. E. H. Tutton, 45°. J. H. Gladstone said that the b.p. is between 170° and 200° ; H. Ritter gave 195° ; E. Baudrimont, 193° ; E. Berger, 189·5° at 774 mm. ; T. E. Thorpe and A. E. H. Tutton, 195° at 760 mm. ; and P. Walden, 193° at 758 mm. J. Ogier found the heat of formation of solid phosphoryl bromide from solid phosphorus to be $(P,O,3Br_{liq.})=108$ Cals., and E. Berger, 109·65 Cals. ; while J. Ogier gave $(P,O,3Br_{gas})=120$ Cals., and E. Berger, 120·75 Cals. E. Berger also found $(PBr_{3liq.},O)=64{\cdot}85$ Cals., and for the decomposition by water, 75 Cals. P. Walden said that the liquid is an electrical conductor, and suggested that it contains the tervalent ion $PO^{\cdots}$.

According to J. H. Gladstone, phosphoryl bromide is not miscible with **water,** but is decomposed by that reagent, forming phosphoric and hydrobromic acids ; it is decomposed by **chlorine** with the expulsion of bromine ; **bromine** forms yellow crystals which liquefy and decompose into bromine and phosphoryl bromide. E. Baudrimont found that **hydrogen sulphide** converts phosphoryl into thiophosphoryl bromide ; and A. Stock, that liquid hydrogen sulphide dissolves phosphoryl bromide, and on evaporating the soln. thiophosphoryl bromide remains, while if the soln. be allowed to remain for some time in contact with phosphorus pentoxide before it is evaporated, some phosphorus pentasulphide is formed. E. Baudrimont found that **phosphorus** does not attack heated phosphoryl bromide ; that **antimony** is brominated ; and that the products of the reaction with **antimony trichloride** are phosphoryl chloride, phosphorus sulphide and tribromide, and antimony tribromide and oxybromide. Ethyl bromide is produced by the action of **alcohol** on phosphoryl bromide. J. H. Gladstone said that **metals** are not attacked ; but, added E. Baudrimont, **tin** is brominated.

A. Michaelis did not succeed in making *pyrophosphoryl bromide,* $P_2O_3Br_4$, by the action of nitrogen peroxide or trioxide on phosphorus tribromide—the products are phosphorus pentoxide and phosphoryl bromide. T. E. Thorpe and A. E. H. Tutton said *metaphosphoryl bromide,* PO_2Br, is produced by the action of bromine on phosphorous oxide as indicated above, and it remains as a residue after the phosphoryl bromide has been removed by distillation.

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§ 35. The Phosphorus Iodides and Oxyiodides

The observations of C. L. Gazzaniga,[1] A. Schrötter, and T. S. Traill were treated in connection with the action of iodine on phosphorus. Some indefinite iodides were mentioned by F. Wöhler, J. L. Gay Lussac, C. M. van Dijk, R. Boulouch, K. I. Lissenko, and F. Sestini. The two best defined iodides are the diiodide and triiodide ; while the existence of the tetritaiodide, the tetratritaiodide, and of the pentaiodide is not so well established. According to R. Boulouch, where dry iodine is added to a soln. of phosphorus in dry carbon disulphide in quantity less than is necessary to convert the phosphorus into the diiodide, and the mixture is exposed to sunlight, **phosphorus tetritaiodide,** P_4I, separates. This is an amorphous, red powder; it decomposes without melting, forming phosphorus diiodide (which dissociates) and phosphorus vapour, and is only slowly attacked by water. Dil. nitric acid attacks the tetritaiodide vigorously, liberating iodine, and with conc. nitric acid, it inflames. Conc. soln. of the alkali hydroxide dissolve it, liberating hydrogen phosphide, and dil. soln. of the alkali hydroxides or carbonates convert it into P_4OH. Phosphorus tetritaiodide dissolves in soln. of iodine, forming phosphorus diiodide or triiodide; this reaction serves to distinguish it from red phosphorus. A. Siemens considers that the alleged tetritiodide is nothing but red phosphorus contaminated with a little diiodide. A. Besson assumed the formation of *phosphorus tritatetraiodide*, P_3I_4, in the preparation of red phosphorus by the action of yellow phosphorus on a soln. of iodine in carbon tetrachloride. The hypothetical compound is supposed to decompose in light $P_3I_4=P_2I_4+P_{red}$.

J. L. Gay Lussac said that on bringing together one part of phosphorus and 16 parts of iodine, a grey-black crystallized substance, fusible at 29°, is formed, and producing on contact with water a colourless soln. containing hydriodic and phosphorous acids; while one part of phosphorus with 24 parts of iodine gave a black substance, fusible in part, at 46°, and dissolving in water with elevation of temp., the soln. containing hydriodic and phosphoric acids, and exhibiting a dark brown colour from the presence of free iodine. F. Hampton said that there is evidence of the formation of **phosphorus pentaiodide,** PI_5, when the two elements are brought together in an atm. of nitrogen; but it is difficult to regulate the violence of the reaction; but if carbon disulphide is used as a solvent for the phosphorus before adding iodine, the process is more manageable.

The formation and preparation of phosphorus diiodide.—J. L. Gay Lussac,[2] and C. A. Wurtz obtained phosphorus diiodide, PI_2, or P_2I_4, by fusing together eq. proportions of the constituent elements. H. W. Doughty recommended heating a mixture of 50 grms. of iodine and 4 grms. of red phosphorus in a 250 c.c. flask by a free flame until the contents are melted; and when the mixture has cooled to 60°, adding 2·5 grms. of yellow phosphorus in small pieces at a time. The process is said to be quick and safe. B. Corenwinder made the diiodide by adding an eq. proportion of iodine to a soln. of phosphorus in carbon disulphide. On cooling the liquid to 0°, crystals of the diiodide separate. They are then exposed to a current of dry air to remove the solvent. Modifications of this process were used by B. Franke, M. Berthelot and S. de Luca, and A. Michaelis and M. Pitsch. The process was also recommended by A. Besson, and R. N. Traxler and F. E. E. Germann. H. Ritter obtained the diiodide by the action of a soln. of iodine in acetic acid on phosphorus trichloride; V. Auger and M. Billy, by the action of phosphorus trichloride on magnesium methyliodide: $3PCl_3+4Mg(CH_3)I=P_2I_4+P(CH_3)_4Cl+4MgCl_2$; A. Besson, by reducing a soln. of phosphorus triiodide in carbon disulphide by mercury; A. W. Hofmann, by the action of iodine on phosphine: $8PH_3+5I_2=P_2I_4+6PH_4I$; A. Damoiseau, by the action of hydrogen iodide on ordinary phosphorus; or by allowing phosphorus to stand in contact with conc. hydriodic acid; P. de Wilde, by the action of phosphorus trichloride on phosphonium iodide; A. Besson, by the action of carbonyl chloride or phosphoryl chloride on phosphonium iodide: $4PH_4I+8COCl_2=P_2I_4+8CO+2P+16HCl$; E. and P. Fireman, by the action of phosphorus pentachloride on phosphonium iodide at 135°; T. E. Thorpe and A. E. H. Tutton, by the action of iodine on phosphorous oxide: $5P_4O_6+8I_2=4P_2I_4+6P_2O_5$; A. Besson, by the action of iodine on phosphorus hemioxide in the presence of carbon tetrachloride; and R. Boulouch, by the action of a soln. of iodine on phosphorus tetritaiodide; or by heating the tetritaiodide: $4P_4I=14P+P_2I_4$.

The properties of phosphorus diiodide.—The pale orange-coloured, triclinic crystals were found by A. E. Nordenskjöld to have the axial ratios $a:b:c=1·0365:1:0·6362$, and $\alpha=97° 54'$, $\beta=106° 25'$, and $\gamma=80° 30'$. E. Bamberger and J. Philipp said that the crystals are probably not isomorphous with those of arsenic diiodide. Analyses made by H. Ritter, and B. Corenwinder agree with the formula PI_2, but the vap. density determinations of L. Troost agree with the formula P_2I_4, since at 265° and 59–99 mm. press., he obtained a vap. density between 18·0 and 20·2—theory for P_2O_4 requires 19·4. L. Troost found that in an atm. of nitrogen under diminished press. the diiodide is not decomposed at 265°; but A. Besson said that some decomposition occurs during fusion, and at 100°–120° and 15 mm. press., the sublimate consists of phosphorus triiodide, and there is a residue of red phosphorus. There is therefore some uncertainty in the mol. wt. deduced from the vap. density. The m.p. given by B. Corenwinder, A. Besson, A. Michaelis and M. Pitsch, and E. and P. Fireman is 110°; and J. L. Gay Lussac gave 100°. R. N. Traxler and F. E. E. Germann gave 124·5°, and added that when a little sulphur is present, the m.p. is lowered. J. Ogier found the heat of formation of the solid diiodide from solid phosphorus to be $(P,I_{2solid})=9{\cdot}88$ Cals., and $(P,I_{2gas})=20{\cdot}68$ Cals.

B. Corenwinder noticed that the diiodide is decomposed by **water** into red phosphorus, some phosphine, and hydriodic and phosphorous acids; and A. Gautier said that if water be gradually added to the diiodide the reaction can be symbolized: $P_2I_4+5H_2O=4HI+H_3PO_3+H_3PO_2$, and the soln. remains clear; and with a large proportion of water there is formed a yellow precipitate with the composition P_5H_3O—*vide supra*. K. I. Lissenko, A. Michaelis and M. Pitsch, and A. Stock and co-workers consider A. Gautier's product to be impure hydrogen diphosphide. U. Antony and G. Magri found that 100 parts of liquid **hydrogen sulphide** dissolve 0·09 part of the diiodide with an absorption of heat and the production of a yellow soln. which conducts electricity. Dry hydrogen sulphide does not act on the diiodide at ordinary temp., but L. Ouvrard represented the reaction at 100°: $2P_2I_4+3H_2S=P_4S_3I_2+6HI$; he also represented the reaction with **phosphorus trisulphide**: $P_2S_3+P_2I_4=P_4S_3I_2+I_2$. J. Tarible found that with **boron tribromide**, the complex *phosphorus borotribromodiiodide*, $P_2I_4.2BBr_3$, or $PI_2.BBr_3$, is formed; while G. Gustavson observed that the diiodide does not react with **boron trioxide**. B. Corenwinder said that the diiodide is soluble in **carbon disulphide**. V. Auger showed that **magnesium methyl iodide** reacts with the diiodide, forming tetramethylphosphonium iodide; and **methyl, ethyl, or propyl iodide,** form iodides of the alkyl phosphines. V. Dessaignes found that **tartaric acid** and water react with the diiodide at 100°, forming malic acid and then succinic acid, but over 120°, gaseous products are obtained. A. Granger found that when the diiodide is heated to 275°–300° in a sealed tube with **mercury,** or when the vapour of the diiodide is passed over mercury at 250°, or when the diiodide is treated with mercury, normal mercuric phosphide is produced. A. Gautier showed that the diiodide reacts with **silver chloride** at ordinary temp.: $6AgCl+3PI_2=3PCl_3+6AgI$; and A. Besson represented the reaction with **mercurous chloride** by a similar equation.

The formation and preparation of phosphorus triiodide.—F. Sestini, R. N. Traxler and F. E. E. Germann, and B. Corenwinder prepared **phosphorus triiodide,** PI_3, adding 12 parts of iodine to a soln. of one part of phosphorus in carbon disulphide, evaporating the liquid out of contact with air, and cooling the syrupy liquid by means of a freezing mixture of ice and salt. The red crystalline plates can be freed from the solvent by a current of air at 50°–60°. L. Ouvrard used this process. A. Besson said that the ready solubility of the triiodide in this solvent makes the process an unfavourable one, and the product has not a high degree of purity. P. Hautefeuille prepared the triiodide by the action of dry hydrogen iodide on dry phosphorus trichloride at ordinary temp., and A. Besson recommended this process, using hydrogen iodide and phosphorus trichloride alone or in the presence of carbon tetrachloride as a solvent. H. L. Snape made the triiodide by heating dry phosphorus trichloride and potassium iodide—with oxygen excluded—in a sealed tube; A. Besson, by the action of hydrogen iodide on phosphoryl choride; L. Ouvrard, by heating the thiophosphoryl iodide: $3P_2SI_4=P_2S_3+4PI_3$; A. Besson, by the action of hydrogen iodide on thiophosphoryl chloride: $PSCl_3+5HI=PI_3+I_2+H_2S+3HCl$, by the action of iodine dissolved in carbon tetrachloride on phosphorus hemioxide, and as a sublimate by heating the diiodide under reduced press.—*vide supra;* R. Boulouch, by the action of a soln. of iodine on phosphorus tetritaiodide; and E. and P. Fireman, by heating phosphorus pentachloride with phosphonium iodide: $3PCl_5+3PH_4I=PI_3+PCl_3+12HCl+4P$.

The properties of phosphorus triiodide.—The deep red tabular or columnar crystals were found by A. E. Nordenskjöld to belong to the hexagonal system and to have the axial ratio $a:b=1:1{\cdot}1009$. The analyses by B. Corenwinder, and A. Besson, and the vap. density determination by L. Troost, agree with the formula PI_3. The vap. density at 250° under diminished press. was 14·32–14·61 when the theoretical value was 14·29. F. M. Jäger gave for the surface tension of the molten triiodide 56·5 dynes per cm. at 75·3°; 55·5 at 99·9°; 53·6 at 121·4°; and 51·4 at 150°. B. Corenwinder, L. Ouvrard, F. M. Jäger, and H. L. Snape gave 55° for the m.p.; and A. Besson, and R. N. Traxler and F. E. E. Germann, 61°. By the application of some arbitrary assumptions of F. M. Flawitzky, A. M. Wasiléeff inferred that the triiodide is a eutectic of the diiodide and iodine. B. Corenwinder said that the triiodide boils with the escape of iodine; and L. Ouvrard found that decomposition occurs when the compound volatilizes. A. Besson, however, said that the compound can be sublimed between 100° and 120° at 15 mm. press., but at a higher temp., iodine is set free. M. Berthelot found that the heat of formation of the solid triiodide from solid phosphorus is $(P,3I_{gas})=26{\cdot}7$ Cals.; $(P,3I_{solid})=10{\cdot}5$ Cals.; and J. Ogier gave $(P,3I)=10{\cdot}9$ Cals. H. Schlundt found the dielectric constant of the solid triiodide to be 3·66 at 20°; and for the liquid, 4·12 at 65°.

B. Corenwinder said that phosphorus triiodide is decomposed by moist **air,** and, added L. Ouvrard, this more easily than is the case with the diiodide. B. Corenwinder found that the triiodide reacts with **water,** forming hydriodic and phosphorous acids and a yellow solid; and A. Besson also found that iodine or some other solid separates out. J. H. Gladstone found that the triiodide is converted by **chlorine** into the trichloride. R. Hanslian discussed the mol. wt. from the effect on the f.p. and b.p. of **iodine.** With a soln. of **sulphur** in carbon disulphide, T. Karantassis observed the formation of **phosphorus tetracosithiotriiodide,** $PI_3.3S_8$. L. Ouvrard represented the reaction with dry **hydrogen sulphide** on the molten triiodide by the equation: $2PI_3+2H_2S=4HI+P_2S_2I_2$; and at 150°, by $2PI_3+3H_2S=P_2S_3+6HI$. C. Hugot observed that the reaction with liquid **ammonia** above −65° agrees with: $PI_3+15NH_3=P(NH_2)_3+3NH_4(NH_3)_3I$; and the triamide is slowly resolved into the imide, $P_2(NH)_3$. L. Ouvrard represented the reaction with **phosphorus trisulphide**; $2P_2S_3+2PI_3=3P_2S_2I_2$, and with an excess of the triiodide: $P_2S_3+4PI_3=3P_2SI_4$. T. Karantassis found that phosphorus triiodide undergoes double decomposition with **arsenic trichloride, antimony tri- and penta-chlorides, bismuth chloride, stannic chloride,** and **lead chloride,** but the corresponding reverse reactions do not occur. No reaction was observed between phosphorus triiodide and **silicon or zirconium tetrachloride.** It is concluded that the iodides of the tervalent metalloids of low at. wt. undergo double decomposition with the bromides or chlorides of higher at. wt. G. Gustavson observed no reaction with **boron trioxide**; and J. Tarible found that with **boron tribromide,** the triiodide forms *phosphorus borotribromodiiodide,* $2PI_3+2BBr_3=P_2I_4.2BBr_3+I_2$. The triiodide was found by A. Besson, and L. Ouvrard to be readily soluble in **carbon disulphide.** J. W. Walker and F. M. G. Johnson represented the reaction with **methyl, ethyl, or n-propyl alcohol** by an equation of the type: $PI_3+3C_2H_5OH=2C_2H_5I+HI+P(OH)_2(OC_2H_5)$. A. Besson said that a soln. of the triiodide in carbon disulphide is reduced by **mercury** in the cold, forming the diiodide, and if the mercury is in excess, mercurous iodide and mercury iodophosphide are formed. J. H. Gladstone added that when the triiodide is distilled with **mercuric chloride,** phosphorus trichloride is formed.

P. Lemoult obtained **phosphorus trisiodomercuriate,** $P(HgI)_3$, by the action of phosphine, diluted with hydrogen or carbon dioxide, on a dil. soln. of potassium iodomercuriate. The product is washed and dried in vacuo. It is slowly decomposed by warm water; and rapidly by alkali-lye. Nitric acid and aqua regia decompose it violently. F. Venturoli prepared yellow **phosphorus iodobisiodomercuriate,** $I.P:(HgI)_2$, by the action of phosphorus on an alcoholic soln. of potassium iodide. The product is decomposed by heat into phosphorus, and mercurous and mercuric iodides.

The phosphorus oxyiodides.—A. Besson suggested that a small quantity of a phosphorus oxyiodide is formed when hydrogen iodide acts on phosphoryl chloride because the resulting phosphorus triiodide gives a relatively small quantity of yellow crystalline plates when decomposed by cold water. According to S. Burton, an oxyiodide with the composition $P_3I_6O_8$ is found in the residue left in the retort in the preparation of ethyl iodide, and may be separated by treating the residue with water, filtering, and evaporating, whereupon it is deposited in red granular crystals, which may be purified by recrystallization. It dissolves readily in water, alcohol, and ether, forming colourless soln. It melts at 140°, and at a higher temp. gives off yellowish vapours, which turn starch-iodide test-paper blue, and condense on a cold surface as a yellowish-red crystalline deposit, exhibiting all the characters of the original substance, which therefore partly sublimes unaltered. Another oxyiodide with the composition PI_2O_2, or $P_4I_8O_8$, was observed in the residue from the preparation of fuming hydriodic acid, and also in the residue from the preparation of methyl iodide.

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§ 36. The Mixed Halides and Oxyhalides of Phosphorus

A number of mixed halides of phosphorus have been reported. H. Moissan[1] observed that phosphorus trifluoride unites additively with chlorine, forming the mixed pentahalide, **phosphorus trifluodichloride,** PF_3Cl_2; and C. Poulenc recommended the following mode of preparation. Two half-litre flasks, provided with leading tubes from the upper and lower parts, and filled with chlorine and phosphorus trifluoride respectively, are connected in such manner that the fluoride can be displaced by mercury into the upper part of the chlorine flask. The gases contract to half their original volume, in accord with the equation $PF_3+Cl_2=PF_3Cl_2$, so that the operation is complete when the whole of the fluoride has been transferred. The mixture is left alone for some days; it must not be shaken with mercury, as it is slowly attacked by it even in the cold. The trifluodichloride is a colourless, non-inflammable gas with a sharp, irritating odour. Its vap. density, 5·39–5·42, is in agreement with 5·46 calculated for PF_3Cl_2. It liquefies under ordinary press. at —8°; and it is decomposed by heating it to 200°–250°, or by the passage of electric sparks: $5PF_3Cl_2=3PF_5+2PCl_5$. With hydrogen, at 250°, it forms phosphorus trifluoride and hydrogen chloride. A small proportion of water decomposed it: $PF_3Cl_2+H_2O=POF_3+2HCl$; and with a larger proportion, the oxyfluoride is decomposed: $POF_3+3H_2O=H_3PO_4+3HF$. It is instantly absorbed and decomposed by alkali-lye. It reacts with sulphur at 115°, forming sulphur monochloride and thiophosphoryl fluoride (*q.v.*). When ammonia is brought in contact with the gas, a white cloud appears and condenses on the walls of the containing vessel—it is phosphorus trifluodiamide; with phosphorus at 120°. This compound is decomposed, forming phosphorus trifluoride and trichloride. Absolute alcohol absorbs the gas, forming a liquid which is a mixture of ethyl chloride and fluoride and some phosphorous acid. The gas is completely absorbed by sodium; while magnesium, mercury, aluminium, tin, lead, iron, and nickel attack it at 180°, forming the metal chlorides, and liberating phosphorus trifluoride.

H. Moissan found that bromine rapidly absorbs phosphorus trifluoride, and if the trifluoride be in excess, the liquid is almost decolorized and **phosphorus trifluodibromide,** PF_3Br_2, is produced. In preparing this compound, the bromine should be cooled by a freezing mixture. Phosphorus trifluobromide is a pale brown, mobile liquid which fumes strongly in air, attacking the respiratory organs. The liquid freezes to a pale yellow crystalline solid at —20°, which melts immediately the freezing mixture is removed. When the liquid is kept at about 15° it soon begins to decompose, giving off bubbles of gas and forming crystals of phosphorus pentabromide: $5PF_3Br_2=3PF_5+2PBr_5$. The compound is vigorously decomposed by water: $PF_3Br_2+4H_2O=H_3PO_4+3HF+2HBr$. It does not attack glass. H. Moissan also found that iodine absorbs phosphorus trifluoride, forming at 300°–400° a yellowish-red solid—possibly **phosphorus trifluodiiodide,** PF_3I_2. The glass containing vessel is at the same time attacked.

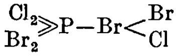
The action of bromine on phosphorus trichloride was first investigated by J. H. Gladstone[2] in an attempt to prepare a chlorobromide. He found that when bromine was poured into phosphorus trichloride, it sank to the bottom and two layers were formed, the upper consisting of a soln. of bromine in the trichloride and the lower of a soln. of the trichloride in bromine. These two layers could not be made to mix, but on adding a little iodine combination immediately took place with development of much heat, and, on cooling, red, crystalline masses separated, resembling phosphorus pentabromide with excess of bromine. The reaction was probably $PCl_3+Br_5I=PBr_5+ICl_3$. He tried other methods for preparing the complex compound, but without success. H. Wichelhaus said that phosphorus trichloride and bromine unite with the development of heat, and the well-cooled mixture deposits crystals of **phosphorus trichlorodibromide,** PCl_3Br_2, but at ordinary temp., the liquid separates into two layers. C. Friedel and A. Ladenburg found an equimolar mixture of phosphorus trichloride and bromine behaved as if it were a trichlorodibromide. A. Michaelis prepared the trichlorodibromide by keeping an eq. mixture of the trichloride and bromine in a sealed tube at a winter's temp. for some time ; the compound decomposed into its components at 35°. A. L. Stern also showed that the trichlorobromide is the first product of the action of the trichloride on bromine.

A. Michaelis said that the trichlorodibromide has the appearance of phosphorus pentabromide. It decomposes about 35° into phosphorus trichloride and bromine, and these components re-unite at a lower temp. The compound is decomposed by water ; H. Wichelaus represented the reaction : $PCl_3Br_2+H_2O=PCl_3+HOBr+HBr$; followed by $HOBr+PCl_3=HCl+POBrCl_2$; while A. Geuther and A. Michaelis represented the reaction by $3PCl_3Br_2+3H_2O=2POCl_3+POBr_3+3HCl+3HBr$. A. Michaelis found that with a soln. of bromine in phosphorus trichloride, it forms trichlorotetrabromide ; and when treated with sulphur dioxide, $PCl_3Br_2+SO_2=POCl_3+SOBr_2$, followed by $2SOBr_2=SO_2+SBr_4$. When the product of the reaction is distilled, bromine and phosphoryl chloride pass over, and a black product, probably sulphur monobromide, remains. G. Gustavson found that with boric oxide boron trichloride and bromine are formed as in the case of phosphorus pentachloride ; H. Wichelhaus, and C. Friedel and A. Ladenburg found that the trichlorodibromide reacts like the pentachloride towards hydroxylic organic compounds ; and A. Geuther represented the reaction with acetic acid : $3PCl_3Br_2+3CH_3COOH=3CH_3COCl+POBr_3+2POCl_3+3HBr$. H. Wichelhaus regarded the trichlorodibromide as a molecular compound of phosphorus trichloride and bromine, but this does not harmonize well with the thermal decomposition $5PCl_3Br_2=3PCl_5+2PBr_5$; and, as pointed out by A. Michaelis, its reactions do not agree with the assumption that it is a mixture of phosphorus pentachloride and pentabromide.

A. L. Stern concluded from his study of the action of bromine on phosphorus trichloride that when bromine is added to phosphorus trichloride, two atoms of bromine may be made to unite with one mol of the chloride, forming the chlorobromide ; when more bromine is added one atom of chlorine in this is displaced by bromine, forming **phosphorus dichlorotribromide,** PCl_2Br_3 ; and still more bromine being added, this compound unites with part of it, forming phosphorus dichloropentabromide, PCl_2Br_5, and at a lower temp. with still more bromine. The number of atoms of halogen with which one atom of phosphorus can combine depends on the temp. : thus phosphorus in presence of 15 gram-atoms of halogen at temp. 13°–15° can combine with only 7 atoms, whereas phosphorus in the presence of 11 gram-atoms of halogen united with 10 gram-atoms to form a compound dissociating above 10°. All the chlorine in the trichloride cannot be displaced by the unaided action of bromine, even if such a large excess as 12 gram-atoms of bromine to 1 mol of phosphorus trichloride be allowed to react for a month ; the presence of a small quantity of iodine, however, will enable a much larger quantity of the chlorine to be displaced.

M. Prinvault reported that yellow crystals of **phosphorus tetrachlorobromide,** PCl_4Br, separate when a cold soln. of the dibromoheptabromide in phosphorus trichloride is heated to its b.p. ; and this compound is also formed by the action of bromine chloride on phosphorus trichloride. He said that the yellow crystals can be regarded as a mol. compound $PCl_3.BrCl$. While the three bromochlorides, PCl_4Br, PCl_3Br_2, and PCl_2Br_3, can be regarded as substitution derivatives of phosphorus pentachloride, or pentabromide. Compounds corresponding with the heptahalide—for example, **phosphorus dichloropentabromide,** PCl_2Br_5, prepared by A. L. Stern, *vide supra ;* and PCl_3Br_4, *vide infra ;* with the unknown enneahalide, *e.g.* PCl_2Br_7 ; with the unknown henahalide, *e.g.* PCl_3Br_8—have been reported.

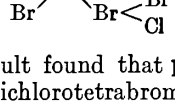
The *phosphorus trichloropentabromide*, PCl_3Br_5, of A. Michaelis is very doubtful. It was said to be formed by adding bromine to an excess of phosphorus trichloride. It may be a supersaturated soln. of ordinary trichlorodibromide in bromine; when the trichlorodibromide is added to the alleged compound, **phosphorus trichlorotetrabromide,** PCl_3Br_4, is produced. A. Michaelis obtained the trichlorotetrabromide by adding bromine to an excess of phosphorus trichloride, and seeding the liquid with a crystal of the desired compound; he also found that in a mixture of phosphorus trichloride and bromine, the lower layer immediately solidified, the trichlorotetrabromide separated out, just as a supersaturated soln. solidifies when a crystal of the salt is dropped into it. M. Prinvault obtained this compound by allowing a mixture of equimolar parts of phosphorus trichloride and trichloroctobromide to stand for some days in a sealed tube. He represented the reaction: $PCl_3Br_8+PCl_3=2PCl_3Br_4$; he also obtained it by dissolving the dichloroheptabromide and then the trichloroctobromide in phosphorus trichloride, and allowing the soln. to stand for some days; and also by the reaction: $PCl_4Br+PCl_2Br_7=2PCl_3Br_4$. The ruby-red prismatic crystals of the trichlorotetrabromide have a blue lustre. The crystals were found by A. Michaelis to be always contaminated with adsorbed bromine, or phosphorus trichloride. The formula agrees with the analyses of A. Michaelis, and M. Prinvault. The former regarded these chlorobromides as mol. compounds of phosphorus trichloride and bromine monochloride. As A. L. Stern pointed out, A. Michaelis' hypothesis is untenable in view of the displacement of the chlorine of the trichloride by bromine; A. Geuther represented the at. structure of the trichlorotetrabromide by



$$\begin{matrix}Cl_2\\Br_2\end{matrix}\!\geqslant\! P-Br\!<\!\begin{matrix}Br\\Cl\end{matrix}$$

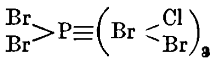
M. Prinvault found that the trichlorotetrabromide decomposes at 60° when heated in a sealed tube: $2PCl_3Br_4=PCl_3+PCl_3Br_8$; when the tube is cooled, the reaction is reversed in a few days' time. A. Michaelis said that the crystals melt when heated, forming two liquid layers which re-unite on cooling to form crystals of the original salt. The compound is decomposed by a small proportion of water into phosphoryl chloride and bromide, hydrochloric and hydrobromic acids, and free bromine; and by a large proportion of water into phosphoric, hydrochloric, and hydrobromic acids and free bromine as recorded by M. Prinvault. A. Michaelis showed that the compound is not altered when shaken with phosphorus trichloride, and it reacts with sulphur dioxide: $2PCl_3Br_4+SO_2=2POCl_3+SBr_4+2Br_2$.

According to M. Prinvault, when phosphorus trichloroctobromide is rapidly distilled above 90°, crystals of **phosphorus dichloroheptabromide,** PCl_2Br_7, appear in the receiver. It was also formed by adding phosphorus trichloride to bromine; there is a vigorous reaction, and after some time, the mixed liquids deposit crystals of this compound. The crystals are said to be very unstable; and to be decomposed by dry air, by carbon disulphide, and by warming them—phosphorus pentabromide and bromine monochloride are formed. The compound dissolves in phosphorus trichloride, and when the soln. is heated to its b.p., phosphorus tetrachlorobromide is formed as indicated above. The dichloroheptabromide is decomposed by water into bromine, and phosphoric, hydrochloric, and hydrobromic acids. M. Prinvault considered it to be a mol. compound $PBr_5.2BrCl$; but A. L. Stern said that M. Prinvault's hypothesis is untenable because compounds are known with less than 5 atoms of bromine to one of phosphorus. A. Geuther supposed that it has the atomic structure



As just indicated, M. Prinvault found that **phosphorus trichloroctobromide,** PCl_3Br_8, is produced when the trichlorotetrabromide is heated in a sealed tube to

60°. He also found that when the homogeneous liquid obtained by adding bromine to phosphorus trichloride is heated on a water-bath at 65° until bromine is no longer evolved, the red liquid which remains forms brown needles at —4° to —5°. A. Michaelis heated a mixture of two mols of bromine with one mol of phosphorus trichloride, and obtained an oily liquid which, on cooling, furnished brown needles with a green reflex. Analyses of the brown acicular crystals agree with the above formula. A. Michaelis found that the compound melts at about 25°, re-forming the original salt on cooling. M. Prinvault said that the compound can be distilled below 90° without decomposition, but above that temp. it forms dichloroheptabromide; while A. Michaelis said that the compound cannot be distilled without decomposition, and that the vapour has the colour of free bromine. M. Prinvault observed that water decomposes the compound into bromine, and phosphoric, hydrochloric, and hydrobromic acids; A. Michaelis found that at ordinary temp. the trichloroctobromide reacts very slowly with sulphur dioxide, but when heated on a water-bath, bromine, phosphoryl chloride, and sulphur bromide are rapidly formed. M. Prinvault said that the compound is soluble in carbon disulphide, and sparingly soluble in phosphorus trichloride with which it forms phosphorus trichlorotetrabromide; A. Michaelis made some observations on this subject—*vide supra*, phosphorus trichloropentabromide. M. Prinvault regarded this substance as a mol. compound of PBr_4 and 3BrCl; and A. Michaelis as a mol. compound of $PCl_3Br_2.3Br_2$. A. Geuther regarded this compound as having the structure:



$$\begin{matrix}\text{Br}\\\text{Br}\end{matrix}\!>\!\text{P}\equiv\left(\text{Br}<\begin{matrix}\text{Cl}\\\text{Br}\end{matrix}\right)_3$$

C. G. Moot[3] reported what was probably **phosphorus trichlorodiiodide,** PCl_3I_2, though the analysis corresponded with PCl_3I. It was obtained by adding an excess of iodine to phosphorus trichloride, and allowing the mixture to stand a few days. The crystals were dried in a current of air, and recrystallized from carbon disulphide. The red, six-sided crystals are decomposed by moist air, and they are very hygroscopic. They decompose at 259° with the separation of iodine. E. Baudrimont prepared **phosphorus hexachloroiodide,** PCl_6I, or $PCl_5.ICl$, by the action of iodine mono- or tri-chloride on phosphorus pentachloride: $PCl_5+ICl_3=PCl_5.ICl+Cl_2$; by direct addition of iodine trichloride and phosphorus trichloride; and by the action of iodine on phosphorus pentachloride: $3PCl_5+I_2=2PCl_6I+PCl_3$. The compound sublimes at about 200°, furnishing orange-red needles or plates. Its vap. density is 4·993 at 260° when the theoretical value for the undecomposed compound is 12·8 and for the compound, when dissociated: $PCl_5.ICl=ICl+Cl_2+PCl_3$, it is 4·27. The compound fumes in moist air, and deliquesces rapidly; it is decomposed by water: $PCl_5ICl+4H_2O=H_3PO_4+5HCl+ICl$.

A series of phosphoryl chlorobromides has been reported, including, with the terminal members, $POCl_3$, $POCl_2Br$, $POClBr_2$, and $POBr_3$. N. Menschutkin[4] reported **phosphoryl dichlorobromide,** $POCl_2Br$, to be formed by treating phosphoryl ethylchloride, $PO(C_2H_5)Cl_2$, with bromine drop by drop. The more volatile ethyl bromide so produced can be separated by fractional distillation from the phosphoryl dichlorobromide—phosphoryl ethylchloride is produced by the action of phosphorus trichloride on alcohol. Other phosphoryl alkylchlorides gave a similar product. According to H. Wichelhaus, phosphoryl dichlorobromide is produced by the action of bromine on a mixture of benzoic acid and phosphorus trichloride when phosphorus trichlorodibromide is first formed: $PCl_3Br_2+C_6H_5.COOH=POCl_2Br+HBr+C_6H_5COCl$; but A. Geuther and A. Michaelis, and K. Kraut did not succeed in confirming this result, and they represented the reaction $3PCl_3Br_2+3C_6H_5COOH=2POCl_3+POBr_3+3C_6H_5COCl+3HBr$ as in the analogous case with water—*vide supra*. A. Besson said that the dichlorobromide is formed when the chlorodibromide is heated to its b.p.: $2POClBr_2=POCl_2Br+POBr_3$; and when a mixture of hydrogen bromide and the vapour of phosphoryl chloride is passed through a glass tube at 400°–500°; at the same time there are formed phosphoryl chlorodibromide, and bromide. These can be separated by fractional distillation. A. Geuther and A. Michaelis obtained it by the action of phosphorus pentabromide on pyrophosphoryl chloride: $PBr_5+P_2O_3Cl_4=2POBrCl_2+POBr_3$; and A. Geuther and O. Hergt, by the action of the pentabromide on phosphorus ethoxydichloride: $P(OC_2H_5)Cl_2+PBr_5=POCl_2Br+PBr_3+C_2H_5Br$, or on phosphoryl ethoxydichloride; $PO(OC_2H_5)Cl_2+PBr_5=POCl_2Br+POBr_3+C_2H_5Br$. Analyses by N. Menschutkin, and H. Wichelhaus agree with the above formula; and N. Menschutkin's value 7·52 for the vap. density agrees with the value 6·86 calculated for $POCl_2Br$. Phosphoryl dichlorobromide is a pale yellow, refracting liquid which, according to A. Geuther and A. Michaelis, freezes to colourless, tabular crystals at 0°, and the solid melts at 11°. A. Besson gave 13° for the m.p., and added that the liquid is very readily undercooled, and that crystallization is then induced by seeding with the dichlorobromide or the chlorodibromide. N. Menschutkin gave 2·059 for the sp. gr. at 0°; T. E. Thorpe, 2·12065 at 0°, and 1·83844 at 137·6° and the mol. vol. at the b.p. is 107·38. If the vol. at 0° is unity, that at the b.p. is 1·15894. He represented the vol., v, at $\theta°$, by $v=1+0·001005180\theta+0·0_6490530\theta^2+0·0_4440650\theta^3$. N. Menschutkin gave 137° for the b.p.; A. Besson, 135°–138°; and T. E. Thorpe, 137·6°. O. Masson, and J. A. Groshans studied the mol. vols. of the family of halides. E. Chambon, and A. Besson found that when fractionally distilled, or when heated in a sealed tube at 185°, phosphoryl dichlorobromide is decomposed into phosphoryl chloride and bromide. N. Menschutkin showed the dichlorobromide is decomposed by water, forming phosphoric acid; and E. Chambon, that phosphorous acid yields a mixture of hydrochloric, metaphosphoric, and orthophosphoric acids.

As indicated above, A. Besson obtained **phosphoryl chlorodibromide**, $POClBr_2$, by fractional distillation from the products of the action of dry hydrogen bromide on the vapour of phosphoryl chloride at 400°–500°. The solid melts at 30°; boils at 165°; and the sp. gr. at 50° is 2·45. As in the case of the dichlorobromide, it shows a great tendency to undercooling, and crystallization can then be induced by seeding with the dichlorobromide or the chlorodibromide. The compound fumes in air, and is at the same time slowly decomposed; with water it forms a mixture of phosphoric, hydrochloric, and hydrobromic acids. When the liquid is boiled in contact with air, the bromine is partially displaced by oxygen, and the product contains phosphoryl chloride, bromide, and dichlorobromide. When heated in a sealed tube, the reactions are: $2POClBr_2=POCl_2Br+POBr_3$; and $3POClBr_2=POCl_3+2POBr_3$.

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§ 37. The Phosphorus Sulphides

The history of the compounds of phosphorus and sulphur is truly a comedy of errors. Compounds diligently investigated and carefully described by one worker could not be prepared by another worker or else are represented as mixtures.—B. HERSCOVICI.

A. S. Marggraf[1] recognized that the reaction of sulphur with phosphorus is very vigorous at an elevated temp., indeed, when a mixture of the dried elements is heated in a test-tube so much heat is evolved that an explosion may occur. At a lower temp. the fused elements mix in all proportions. Before any test was available as to the individuality of those products quite a large number of phosphorus sulphides was reported by B. Pelletier, M. Faraday, A. Dupré, A. Levol, R. Böttger, J. J. Berzelius, G. Lemoine, etc. These include P_4S, P_4S_2, P_4S_3, PS, P_4S_5, P_8S_{11}, P_2S_3, P_3S_5, P_4S_7, P_3S_6, P_4S_9, P_2S_5, P_2S_6, and P_2S_{12}. J. J. Berzelius, guided largely by the analogy between sulphur and oxygen, said that "phosphorus forms with sulphur a series of compounds precisely analogous in composition to those it forms with oxygen. Moreover, some of these compounds may be obtained in two allotropic forms in one of which the phosphorus appears to exist in its ordinary state, in the other, in its red modifications."

J. J. Berzelius described the preparation of *phosphorus tetritasulphide*, P_4S, by melting eq. proportions of the two elements under water, or on a water-bath ; W. Wicke said that the union may be effected at ordinary temp. A red modification was said to be obtained when the ordinary form, or the hemisulphide, is heated in contact with an electropositive metal sulphide—say sodium sulphide. J. J. Berzelius also described yellow and red forms of *phosphorus hemisulphide*, P_2S, or P_4S_2, obtained in a similar way by using eq. proportions of the two elements. According to H. Schulze, G. Ramme, A. Helff, and F. Isambert, these *hyposulphides* are mixtures of sulphur with red or yellow phosphorus, though G. Lemoine was inclined to regard them as chemical individuals. R. Boulouch reported *phosphorus tetritapentasulphide*, P_4S_5, to be formed by adding a crystal of iodine to a mixed soln. of sulphur (5–7 grms.), and the tetritatrisulphide (23 grms.) in carbon disulphide (200 c.c.). The crystals which separate in a couple of days retain the solvent very tenaciously, and melt at 180°–210°. He added that the sulphide is probably a solid soln. E. Dervin also reported *phosphorus octitahenasulphide*, P_8S_{11}, to be formed when a mixture of the tetritatrisulphide and a carbon disulphide soln. of not enough sulphur to form P_3S_6 is heated in a sealed tube at 180°. The product is separated mechanically from the P_3S_6. The same sulphide was said to be formed by heating the tetritatrisulphide with P_2S_3 or P_2S_5 in the presence of carbon disulphide at 180°. The crystals are not identical with those of P_4S_5, and both E. Dervin, and R. Boulouch believe that the product is probably a solid soln. R. Boulouch reported the formation of *phosphorus tritapentasulphide*, P_3S_5, in small crystals by the action of sulphur on an excess of phosphorus dissolved in carbon disulphide containing a little iodine. This is probably not a chemical individual, but rather a solid soln. The *phosphorus persulphide* or *dodecasulphide*, P_2S_{12}, of J. J. Berzelius, was obtained by dissolving sulphur in liquid hemisulphide. The product appeared in crystals resembling those of sulphur. This product is probably a solid soln. of sulphur in one of the other phosphorus sulphides, although it appears as a maximum on H. Giran's m.p. curve, Fig. 51. A. Dupré's *phosphorus hexasulphide*, P_2S_6, obtained in an analogous manner, is probably a similar solid soln. with less sulphur. G. Ramme apparently so regarded it.

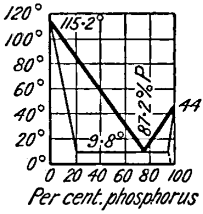
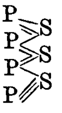
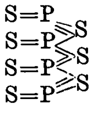


FIG. 51.—Fusion Curve of Mixtures of Phosphorus and Sulphur.

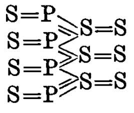
According to R. Boulouch, the f.p. curve of varying proportions of phosphorus and sulphur associated by fusion at temp. below 100° consists of two lines, Fig. 51, which cut sharply at the eutectic temp., 9·8° and 22·8 per cent. of sulphur. Hence, there is no evidence of the formation of a definite compound of the two elements below 100°. Mixed crystals, or solid soln., rich in sulphur are formed, and these are isomorphous with octohedral sulphur ; similarly, mixed crystals, or solid soln., rich in phosphorus, are isomorphous with phosphorus. F. Isambert found that when a mixture of phosphorus, even with a large excess of sulphur, is distilled at 100° in vacuo, all the phosphorus distils over, and a residue of sulphur remains. H. Giran heated mixtures of the two elements in sealed tubes at about 200°, and after cooling, found the temp. at which complete liquefaction occurred. The results are indicated in Fig. 52. The formation of four different compounds is indicated by four temp. maxima on the curves representing the dependence of the liquefaction temperature on the composition. The maximum temp. are 167°, 296°, 272°, and 314°, the corresponding composition being expressed by the formulæ P_4S_3, P_2S_3, P_2S_5, and P_2S_6 respectively. The four eutectics at —40°, +46°, +230°, and +243° correspond approximately with the compositions P_2S, PS, PS_2, and PS_3 respectively. The mixtures of sulphur and phosphorus, which are liquid at the ordinary temp., exhibit super-cooling to a marked degree; solidification can only be brought about by cooling to about —80°. R. Boulouch added that there is not a eutectic at —40° with 33·5 per cent. of sulphur; and he showed that instead of the curve travelling *DCBA*, it travels *DBA* with the eutectic at —7°. The appearance of precision conveyed by Fig. 51 is illusory. The whole subject wants carefully overhauling. A. Stock and H. von Bezold said that the existence of only the following compounds: P_4S_3, P_4S_7, P_3S_6, and P_2S_5 or P_4S_{10} can be regarded as definitely established. Unlike H. Giran, they obtained two maxima between P_2S_5, m.p. 276°, and P_4S_3, m.p. 166°—the one at 303° corresponded with P_4S_7, and the one at 298° with P_3S_6. M. Rudolph, and B. Herscovici also found a maximum at 311°, corresponding with P_4S_8, on the f.p. curve of the binary system P_4S_3–P_2S_5. The —40° observed by H. Giran is probably due to a state of surfusion produced by rapid cooling. R. Boulouch found that the f.p. curve of crystals rich in P_4S_3 consists of two portions at different inclinations, and it is the intersection of the second portion with the curve of solidification of crystals rich in phosphorus which determines the eutectic point. The point of intersection of the two portions of the curve of solidification of crystals rich in P_4S_3 occurs where the conc. of sulphur is 36 per cent. and the temp. 44° (that is, the m.p. of the phosphorus), and ought to be regarded as a transition point. The most probable explanation is that above 44° phosphorus sulphide, P_4S_3, is deposited, and below that temp. a mixture of phosphorus and phosphorus sesquisulphide. A. Gorboff made some observations on the composition of the eutectic. J. Mai represented P_4S_3, P_4S_7, and P_4S_{10} by the following graphic formulæ:



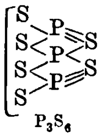
P_4S_3



P_4S_7



P_4S_{10}



P_3S_6

In addition to the numerous compounds reported as a result of the direct union of the elements by fusion, a number have been obtained—by B. Corenwinder, R. Boulouch, A. Seidel, etc.—by crystallization from soln. of phosphorus and sulphur in carbon disulphide. A. Helff said that no compound is formed from soln. of the two elements in carbon disulphide. For A. Delachaux's observations on the production of phosphorus sulphides by the action of hydrogen sulphide or sulphur on phosphine, *vide supra.*

G. Lemoine reported the formation of **phosphorus tetritatrisulphide,** P_4S_2, by heating red phosphorus and sulphur to about 160°; F. Isambert said that yellow phosphorus can be employed if the violence of the reaction be moderated by admixture with sand. Many others have since reported the formation of this compound by the direct union of the elements—*e.g.*, A. Helff, H. von Bezold, G. Ramme, J. Mai and F. Schaffer, E. Scharff, and M. Rudolph. G. Lemoine, H. Rebs, and H. Schulze said that the tetritatrisulphide is also formed by heating the so-called tetritasulphide to about 100°, in an indifferent gas; E. Dervin, by heating the hemitrisulphide or the octitahenasulphide with carbon disulphide in a sealed tube at 200°; and A. Besson, by the action of phosphine on thionyl, sulphuryl, or pyrosulphuryl chloride. H. Giran's curve, Fig. 52, gives an idea of the part played by this compound in the binary system: P–S.

A. Stock and H. von Bezold said that this compound is obtained by heating the calculated amounts of sulphur and red phosphorus in a sealed tube to 180°, and crystallizing the raw materials from alcohol. A. Stock and M. Rudolph recommend the following mode of preparation:

> An excess of red phosphorus is mixed with finely-powdered sulphur, and the mixture heated in a wide tube, sealed at one end, in an atmosphere of carbon dioxide. The temperature is first gradually raised to 100°, and then the reaction started by stronger local heating near the surface of the mixture. When the reaction has spread through the whole mass, the tube is strongly heated until the contents begin to distil, otherwise higher sulphides of phosphorus are formed; the reaction product, which consists of red phosphorus and tetraphosphorus trisulphide, is allowed to cool in the atmosphere of carbon dioxide. The trisulphide may be separated from the red phosphorus by extraction with carbon bisulphide or by distillation in an atm. of carbon dioxide, but in both cases it is somewhat impure.

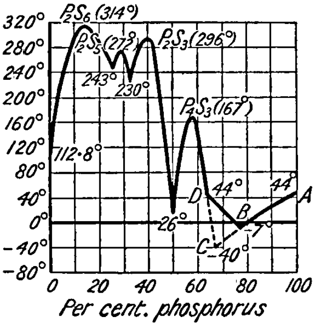


FIG. 52.—Fusion Curve of Mixtures of Phosphorus and Sulphur.

This sulphide occurs in commerce under the name *phosphorus sesquisulphide*, where it is employed in the manufacture of matches. Analyses have been discussed by M. Rudolph, C. T. Mörner, H. Henzerling, J. Mai and F. Schaffer, E. G. Clayton, L. Aronstein, and C. van Eijk. E. G. Clayton found 83·34–97·86 per cent. of P_4S_3; water and volatiles lost at 100°, 0·18–8·74 per cent.; phosphoric acid, 1·23–2·14 per cent.; uncombined sulphur, 0·17–4·17 per cent.; calcium phosphate, up to 3·30 per cent.; calcium sulphate, up to 0·27 per cent.; iron oxide, etc., up to 1·72 per cent.; and silicious matters, up to 0·80 per cent. The objectionable impurity is free phosphorus. J. Mai and F. Schaffer showed that if too high a temp.—say 340°—is employed in its preparation, phosphorus will be present; and if too low a temp. be employed, the substance cannot be conveniently powdered. The crude commercial sulphide, which had been made by gradually heating red phosphorus with some excess of sulphur to a temperature of 330° in a current of carbon dioxide, was heated for 2–3 hours at 180° in a stream of dry carbon dioxide; the evolution of hydrogen phosphide was observed, and the formation of a crystalline sublimate; this was obtained in much larger quantity when the sulphide was heated at 340°. This sublimate was luminescent at 40° when observed in the dark, and at that temperature evolved a white vapour; it melted at 155°–164°, was readily soluble in carbon disulphide, and is undoubtedly phosphorus tetritatrisulphide free from phosphorus. In this state, it melts to an amber-yellow liquid, and not red as is usually stated. A further series of experiments were made with phosphorus sesquisulphide, which had been obtained from the crude product by repeated crystallization from a mixture of carbon disulphide and petroleum. When heated at 40°–50°, it luminesces strongly, emits a white vapour, and becomes slowly oxidized. When boiled with water luminescence continued as long as the water was boiled, but ceased as soon as the boiling was stopped. After prolonged distillation with steam, a minute quantity of solid distillate was obtained which consisted mainly of phosphorus tetritatrisulphide mixed with a small quantity of oxidized substances; the condensed steam contained hydrogen sulphide.

Analyses of the purified compound by G. Lemoine, G. Ramme, H. Schulze, J. Mai and F. Schaffer, L. Wolter, and A. Stock and co-workers are in agreement with the formula P_4S_3. G. Lemoine found that the fractional crystallization and fractional sublimation of the tetritatrisulphide gave no evidence of a heterogeneity. The vap. density determinations of G. Ramme, G. Lemoine, F. Isambert, A. Helff, and A. Stock and H. von Bezold are in agreement with this formula, so also is the mol. wt. calculated from the effect of this sulphide on the b.p. of carbon disulphide by A. Helff, and A. Stock and H. von Bezold. The fused product appears as a yellow crystalline mass, and, according to G. Lemoine, when crystallized from its soln. in carbon disulphide, phosphorus trichloride, or thiophosphoryl chloride, appears in pale yellow, rhombic prisms. G. Lemoine gave 2·1 for the sp. gr.; F. Isambert, 2·00 at 11°; and A. Stock and H. von Bezold, 2·03 at 17°. G. Lemoine found the m.p. to be 142°, but when the sulphide was crystallized from its soln. in carbon disulphide, G. Ramme obtained a much higher value, namely, 166°; F. Isambert gave 167°; H. Rebs, 165°; A. Helff, 165°–166°; J. Mai and F. Schaffer, 155°–164°; and E. Scharff, 167°. H. Giran gave 167°, and added that the presence of an excess of either sulphur or phosphorus depresses the m.p.—Fig. 52. A. Stock and co-workers obtained 171°–172·5° for the m.p. F. Isambert gave 380° for the b.p.; J. Mai and F. Schaffer, 408°–418°; G. Lemoine, 410°–420°; and A. Stock and M. Rudolph, 407°–408° at 760 mm. As indicated above, vap. density determinations by G. Ramme, G. Lemoine, and A. Helff ranging from 7·43 to 8·17 are in agreement with 7·62 (air unity) calculated for the tetritatrisulphide; A. Stock and H. von Bezold obtained:

	700°	750°	800°	850°	900°	950°	1000°
Vap. density .	219	213	202	185	182	179	179

in agreement with the calculated value 220° when the temp. is near 700°; at higher temp., dissociation becomes appreciable. A. Helff, and A. Stock and M. Rudolph found the mol. wt. calculated from the raising of the b.p. of benzene to be 228 to 264 when the theoretical value is 220°. The heat of formation of the tetritatrisulphide is, according to F. Isambert, (4P,3S)=16·4 Cals. He added that since the transformation of ordinary into red phosphorus is accompanied by the production of a greater amount of heat, namely, 20 Cals., the red phosphorus and sulphur ought not to combine directly. The fact that they do combine at an elevated temp., 180°, shows that the vap. press. of red phosphorus at this temp. must be high enough to convert some red phosphorus into ordinary phosphorus at the moment of combination. Even at 260° red phosphorus unites with sulphur only slowly and without an explosion, and then only an insignificant thermal change accompanies the formation of the tetritatrisulphide. A. Stock and F. Gomolka also found the reaction between sulphur and red phosphorus to be slow at 200°.

According to G. Lemoine, air at ordinary temp. has no action on the tetritatrisulphide. This sulphide inflames in air at about 100°, and it can be distilled between 300° and 400°; it can, however, be volatilized completely at 260° in a current of carbon dioxide. A. Stock and M. Rudolph observed a slight decomposition when the molten sulphide is kept for a month in a sealed glass tube, but they added that this may be an effect of the presence of traces of moisture. When distilled, A. Stock and H. von Bezold observed that the distillate was slightly richer in phosphorus—having 44·0 instead of 43·7 per cent. of sulphur; and the residue in the retort slightly richer in sulphur—having 55·8 instead of 56·3 per cent. of phosphorus. R. Böttger, and W. Wicke observed that phosphorus sulphide is decomposed by light.

According to E. Scharff, when the tetritatrisulphide is heated in **air** at 80°, in darkness, a greenish flame hovers over the mass, and a white cloud with a characteristic odour appears; if oxygen be introduced into the vessel, the luminescence is at first intensified, and it then disappears. As with phosphorous oxide, there is a maximum press. favourable for the luminescence. No ozone was detected. Since the tetritatrisulphide at an elevated temp. is partially resolved into ordinary phosphorus, it might be thought that the luminescence is produced by the oxidation of phosphorus or of phosphorous oxide; but J. Mai and F. Schaffer (*vide supra*), and E. G. Clayton agree that the glow is different from that of yellow phosphorus. E. Scharff observed that in **oxygen** at 70° and 368·48 mm. press., there appears abruptly, just over the sulphide, a clear, intermittent luminescent glow which approaches the steady state as the press. diminishes, until at 294·59 mm.

press. the luminescence is continuous; as the press. is increased, the luminescence again becomes intermittent, and vanishes at 387·67 mm. press. The results at different temp. are indicated in Table VIII, for dry and moist oxygen. Normally, the luminosity begins at 65°, and it burns at 90° with a greenish flame, forming phosphoric and sulphurous oxides. The press. at which the luminescence ceases is generally higher than that at which it starts, and the difference is greater, the higher the temp.; and if the press. is again reduced, the luminescence starts at a higher press. than it originally did. The luminescence is not much affected if toluene vapour be also present; and it is feeble in the presence of turpentine, and the intermittent phenomenon persists. Iodobenzene, benzene, chloroform, carbon disulphide, and alcohol give an enfeebled luminescence; and with amylene the sulphide suddenly ignites at 90° without showing the luminescence.

TABLE VIII.—EFFECT OF TEMPERATURE AND PRESSURE ON THE LUMINESCENCE OF PHOSPHORUS TETRITATRISULPHIDE.

Dry oxygen.				Moist oxygen.		
Temp.	Begins.	Steady.	Ends.	Begins.	Steady.	Ends.
65°	264·50	242·05	310·45	274·35	250·27	281·36
70°	386·75	321·85	389·25	368·48	294·59	387·67
75°	483·25	427·05	496·85	481·23	403·95	486·17
80°	558·42	506·05	592·25	633·82	513·74	650·11
85°	627·75	557·85	632·25	766·47	688·01	823·23
90°	661·72	595·75	679·15	—	870·55	—

The tetritatrisulphide was found by G. Lemoine to be but slightly decomposed by cold **water**, while boiling water slowly forms hydrogen sulphide and phosphoric acid—for J. Mai and F. Schaffer's observations with the commercial sulphide, *vide supra*. A. Stock and M. Rudolf said that this sulphide is more stable towards water than any of the other phosphorus sulphides, for it is only gradually decomposed even by boiling water. G. Lemoine said that the sulphide is slowly but completely decomposed by **chlorine** water, forming, according to F. Isambert, phosphoric and sulphuric acids. F. Isambert found that a soln. of **iodine** in carbon disulphide rapidly attacks the tetritatrisulphide yielding phosphorus triiodide, but has no action on compact red phosphorus, a difference due to the fact that the formation of phosphorus triiodide develops less heat than the conversion of ordinary phosphorus into red phosphorus. The phosphorus does not exist in the tetritatrisulphide as red phosphorus, all the latter having been converted into the ordinary variety at the moment of combination. A. Wolter said that by cooling a mixed carbon disulphide soln. of iodine and the tetritatrisulphide, yellow crystals of the iodide $P_4S_3I_2$ are formed. G. Lemoine found that **hydrochloric acid** has scarcely any action in the cold. According to E. Dervin, when two parts of **sulphur** and one of phosphorus tetritatrisulphide are dissolved in carbon disulphide in a sealed tube, and the soln. exposed to the light for one or two months, fine pale-yellow transparent needles of the sulphide, P_3S_6, are formed. This compound is not affected by heating under pressure with carbon disulphide. In the above reaction crystalline spherical grains of P_8S_{11} are also formed. R. Boulouch said that if a crystal of iodine be added to a carbon disulphide soln. of sulphur and phosphorus tetritatrisulphide, phosphorus tetritapentasulphide gradually separates out. G. Lemoine found that **sulphuric acid** has scarcely any action in the cold. According to A. Stock, liquid **ammonia** in a sealed tube forms a reddish-brown soln. which becomes dark red, and finally forms a brown jelly; when the tube is opened phosphine escapes with the excess of ammonia, and there remains a viscid mass containing a thiophosphate and other substances. G. Lemoine said that cold **nitric acid** dissolves the sulphide with the separation of sulphur; **aqua regia** dissolves the sulphide completely. F. Isambert made analogous observations. He also observed that if some tetritatrisulphide be placed on a stick of phosphorus, the latter melts at the point of contact; and if a mixture of **phosphorus** and its tritatrisulphide be heated at 100° in vacuo, phosphorus distils over carrying with it a small portion of the tetritatrisulphide. E. Dervin found that when the tetritatrisulphide is mixed with **phosphorus tetritahexasulphide,** or **phosphorus tetritadecasulphide,** in carbon disulphide soln., and heated to 180° in a sealed tube, the tritahexasulphide and octitahenasulphide are formed. A. Stock and co-workers examined the f.p. curves of mixtures of phosphorus tetritatrisulphide with **phosphorus tetritadecasulphide,** and found two eutectics with a maximum corresponding with phosphorus tetritoctosulphide; while with **phosphorus tetritaheptasulphide** there is only one eutectic. G. Lemoine found that the tetritatrisulphide dissolves in **alcohol,** and **ether** with decomposition. The solubility in **carbon disulphide** was observed by G. Lemoine, and H. Schulze; the former said that 100 parts of the solvent dissolve 60 parts of the tetritatrisulphide, and A. Stock and M. Rudolph gave for the solubility in 100 parts of carbon disulphide at —20°, 0°, and 17°, respectively 11·1, 27·0, and 100 parts of the tetritatrisulphide, while 100 parts of **benzene** at 17° and 80° dissolve respectively 25 and 11·1 parts; and 100 parts of **toluene** at 17° and 111°, dissolve respectively 31·2 and 15·4 parts. The yellow soln. in carbon disulphide gives a broad absorption band from the middle of the blue to the violet. G. Lemoine said that a cold soln. of **potassium hydroxide** acts on the tetritatrisulphide with the development of much heat-forming phosphine, hydrogen, potassium sulphide, and potassium hydrophosphite—*vide infra,* oxythiophosphates. A. Stock and M. Rudolph found that finely-divided phosphorus tetritatrisulphide reacts vigorously with a soln. of potassium hydroxide when hydrogen and phosphine (1 : 1 or 2 : 1) are evolved. At ordinary temp., the evolution of gas lasts for days. If the reddish-brown soln. be acidified immediately after it is prepared, a yellow precipitate resembling hydrogen diphosphide is formed. This precipitate is not formed with soln. that have been kept for some time. According to M. Frouin, when this sulphide is in contact with the moisture of the skin, it evolves hydrogen sulphide; and, probably by reason of the formation of volatile phosphorus compounds, the vapours are said to be more poisonous than those of ordinary phosphorus.

F. A. Kekulé, G. Lemoine, A. Michaelis, and F. Isambert reported *phosphorus trisulphide,* P_2S_3, or **phosphorus tetritahexasulphide,** P_4S_6, to be formed by melting eq. proportions of red phosphorus and sulphur in an atm. of carbon dioxide. J. Mai could not obtain a homogeneous product in this way; and A. Helff said that the product is never homogeneous since the tetritatri- and tetritahepta-sulphides can be separated from the product. According to L. Springer, the loss due to the burning of the mixture of red phosphorus and sulphur in the preparation of phosphorus trisulphide is avoided by at first heating only a small portion of the mixture in a fireclay crucible until combination takes place, removing the burner and then adding the rest of the mixture in small portions at a [time. If the first charge takes fire, it is extinguished by means of sand, and after each subsequent addition the lid is replaced on the crucible. The action takes place quietly, causing only a slight puff and formation of fume. J. J. Berzelius obtained it as a sublimate by heating either the hemisulphide or manganese diphosphodisulphide, MnS.P_2S, and sulphur; H. Schulze, by heating the so-called tetritasulphide and sulphur; G. S. Sérullas, by the action of hydrogen sulphide on phosphorus trichloride—J. H. Gladstone used phosphorus tribromide, and L. Ouvrard, the triiodide; A. Besson, by the action of hydrogen iodide on warm thiophosphoryl chloride; and L. Ouvrard, by heating phosphorus disulphodiiodide in vacuo at 300°, or by treating the same compound with water; and by the decomposition of the sulphotetriodide. F. Krafft and B. Neumann purified it by sublimation in vacuo. The tetritahexasulphide is variously described as a white or yellowish-white crystalline mass. Analyses by H. Schulze, J. J. Berzelius, and L. Ouvrard agree with the empirical formula P_2S_3, and F. Isambert found the vap. density 10·2–12·0 in agreement with 10·9 required for P_4S_6. G. Ramme could not obtain this compound by heating the elements in the presence of carbon disulphide. J. Mai, A. Helff, E. Dervin, R. Boulouch, and A. Stock and co-workers all doubted the existence of this product as a chemical individual. It appears as a maximum on H. Giran's fusion curve, Fig. 51; but A. Stock and co-workers did not verify this.

The following properties have been ascribed to the tetritahexasulphide: H. Schulze said that when heated it becomes orange-yellow, melts, and then sublimes. G. Lemoine said that it fuses at 290°, and F. Giran, 296°. J. J. Berzelius said that it sublimes below the b.p. of sulphur. F. Isambert gave 490° for the b.p., and M. von Recklinghausen, 545°–546·5°. According to J. J. Berzelius, this sulphide does not fume or luminesco in darkness; and J. J. Berzelius, and G. Lemoine found that it is readily decomposed in moist *air*, forming sulphur and phosphoric acid. It burns with a yellowish-white flame when heated in air. F. A. Kekulé, and G. Lemoine found that with *water* it forms hydrogen sulphide and phosphoric acid. A. Michaelis said that with *bromine* it forms a trisulphotetrabromide; and L. Ouvrard, with *iodine* in the presence of carbon disulphide, disulphodiiodide. A. J. Balard found that with *hypochlorous acid* it forms chlorine, and sulphuric, phosphoric, and hydrochloric acids. According to A. Bineau, it absorbs *ammonia* very slowly, and in about 6 months a yellow solid with an hepatic odour is formed. J. J. Berzelius said that the sulphide is soluble in aq. ammonia—*vide infra*, the action of alkali-lye. L. Ouvrard found that it reacts with *phosphorus diiodide:* $P_2S_3+P_2I_4=P_4S_3I_2+2I$, and with *phosphorus triiodide:* $2P_2S_3+2PI_3=3P_2S_2I_2$, or with an excess of the iodide: $P_2S_3+4PI_3=3P_2SI_4$. E. Dervin said that when heated with *phosphorus tetritatrisulphide* in the presence of carbon disulphide at 180°, it forms the so-called pentasulphide, and octitahenasulphide. F. Krafft and B. Neumann observed that with *arscnic* at 240°–300°, arsenic trisulphide and phosphorus are formed; and an analogous reaction occurs with *antimony* at 325°. When heated with *carbon disulphide* under press., it forms the tetritatrisulphide and tritahexasulphide. F. A. Kekulé said that with *acetic acid*, thioacetic acid is formed; and L. H. Friedburg, with *succinic acid*, thiophene is produced. N. Speransky studied its action on *menthone*. J. J. Berzelius found that the tetritahexasulphide is soluble in cold aq. soln. of the *alkali carbonates* with the separation of sulphur; it is also readily soluble in soln. of the *alkali hydroxides*. The pale yellow soln. give with acids a white flocculent precipitate of the original sulphide. G. Lemoine said that the evaporation of the soln. with very dil. alkali-lye yields alkali phosphite: but if the alkali-lyo be in excess, oxythiophosphites are formed. J. J. Berzelius, and L. Ferrand found that it unites with *metal sulphides*, forming thiophosphates.

According to J. Mai, some **phosphorus tetritaheptoxide,** P_4S_7, is formed during the distillation of phosphorus tetritahexasulphide in vacuo under 11 mm. press., at 290°–300°. The product was heated with carbon disulphide in an atm. of carbon dioxide in a sealed tube at 150°–160°. The crystals so formed are pressed between filter-paper, and freed from the solvent by warming them in vacuo. A. Stock and H. von Bezold made it by melting together 2 gram-atoms of red phosphorus and three of sulphur, and extracting the mass with carbon disulphide with a reflux condenser; by heating a soln. of the tetritatrisulphide and the tetritadecasulphide in carbon disulphide at 100°; and A. Stock and B. Herscovici, by heating an intimate mixture of red phosphorus and sulphur in proportions eq. to P_4S_7 with 5 per cent. P_4S_3 is heated in a hard glass tube until distillation begins. The cooled product is then recrystallized from carbon disulphide in which the heptasulphide is sparingly soluble and the trisulphide readily soluble. The pale yellow or colourless, prismatic crystals decompose rapidly in air with the evolution of hydrogen sulphide. This compound, said A. Stock and B. Herscovici, is more sensitive to moisture than is the case with the tetritatrisulphide. The analyses of J. Mai, A. Helff, and A. Stock and co-workers and the vap. press. 11·63–11·71 (air unity) of A. Helff are in agreement with the formula P_4S_7. A. Stock and B. Herscovici found the vap. density up to 700° in agreement with 348 calculated for P_4S_7; but at higher temp. decomposition occurs, and the mol. wt. falls to less than half this value:

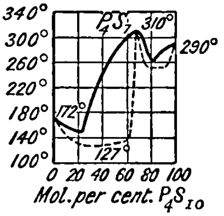


FIG. 53.—Melting-point Curve of Mixtures of P_4S_6 and P_4S_{10}.

	700°	750°	800°	850°	900°	950°	1000°
Mol. wt. . .	337	323	202	193	179	173	167

The sp. ht. is 2·19 at 17°. The sulphide sinters at 305°–308°, and the m.p. is 310°, and it is not changed by repeated extraction with carbon disulphide. It boils at 523° and 760 mm. The m.p. curve of binary mixtures of phosphorus tetritahexa- and tetritadecasulphide is indicated in Fig. 53. The m.p. curve, said A. Stock, has a single maximum at 310° corresponding with P_4S_7, and eutectics at 127° and

47·5 per cent. of sulphur, and 248° and 69 per cent. of sulphur. Although only sparingly soluble in carbon disulphide, this is the best solvent known for this sulphide—100 parts of carbon disulphide dissolve 0·0050 part of the tetritaheptasulphide at 0°, and 0·0286 part at 17°.

A. Seidel prepared *phosphorus disulphide*, or **phosphorus tritahexasulphide,** P_3S_6, by heating the calculated quantities of ordinary phosphorus and sulphur with carbon disulphide in a sealed tube at 210°, and G. Ramme observed its formation when the at. proportions of the phosphorus and sulphur range from 2 : 3 to 1 : 6. The raw product was purified by crystallizing it six times from carbon disulphide in a sealed tube. E. Dervin obtained it by exposing to direct sunlight a soln. of 2 parts of sulphur and one of phosphorus tetritatrisulphide in carbon disulphide; the crystalline precipitate formed needle-like crystals in two months' time. He obtained it by heating the so-called octitahenasulphide with carbon disulphide at 200° in a sealed tube; by heating the tetritatrisulphide and tetritahexasulphide with carbon disulphide at 180°—some octitahenasulphide was formed at the same time; and by heating the tetritahexasulphide with carbon disulphide in a sealed tube—some tetritatrisulphide was formed at the same time. R. Boulouch obtained this sulphide by exposing to sunlight for a couple of days a carbon disulphide soln. of phosphorus with an excess of sulphur in the presence of a crystal of iodine. J. Mai obtained the tritahexasulphide by distilling a molten mixture of sulphur and phosphorus in the proportion 2 : 1; and A. Helff by melting together eq. proportions of the constituent elements. J. Mai added that when an intimate mixture of phosphorus and sulphur in the at. proportion 1 : 2, is heated in an atm. of carbon dioxide, and the product distilled, a yellow crystalline substance, P_4S_3, passes over. The later fractions consist of a mixture of phosphorus tritahexasulphide and tetritadecasulphide which cannot be separated by fractional distillation owing to the close proximity of their b.p. A. Stock obtained no evidence of the existence of this sulphide on the m.p. curve of mixtures of phosphorus tetritatri- and tetritadeca-sulphides, Fig. 53; and H. Giran's result, Fig. 52, is explained by the imperfect equilibrium attained at 200°—he should have employed 300°. H. von Bezold, however, maintained that there is evidence of the formation of this sulphide on the m.p. curve of mixtures of the tetritatri- and tetritadecasulphides, but the compound readily dissociates into the tetritaheptasulphide, etc., on cooling.

The analyses of G. Ramme, J. Mai, E. Dervin, A. Helff, and A. Seidel agree with the empirical formula PS_2; and the vap. density determinations of G. Ramme, and A. Helff agree with the formula P_3S_6, while those of J. Mai agree with P_4S_8. H. von Bezold obtained a result similar to that of J. Mai from mixtures of phosphorus tetritadecasulphide and tetritatri- or tetritaheptasulphide. H. von Bezold's result for the effect of the tritahexasulphide on the b.p. of carbon disulphide agrees with P_3S_6. A. Seidel, G. Ramme, A. Helff, R. Boulouch, and E. Dervin agree that the compound forms pale yellow,. transparent, needle-like crystals. J. Mai said that this sulphide easily decomposes, and after it has been in a desiccator for a short time, there is a separation of sulphur. A. Seidel gave 248°–249° for the m.p.; G. Ramme, and A. Helff, 296°–298°; E. Dervin, 296°; and H. von Bezold, 298°. J. Mai found that at 10–11 mm. press., this sulphide gives a pale green vapour between 335°–340°, and the distillate has the composition P_3S_9. M. von Recklinghausen gave 516°–519° for the b.p. J. Mai said that phosphorus tritahexasulphide readily decomposes; and G. Ramme, that when heated with water for 5–6 hrs. in a sealed tube, hydrogen sulphide and phosphorous and phosphoric acids are formed, while a residue remains which is not soluble in carbon disulphide, and which does not melt at 310°. When heated with phosphorus, the tetritatrisulphide is formed. This sulphide was found by A. Stock to dissolve in liquid ammonia, forming a brown soln. which after some time deposits crystals of ammonium amidothiophosphate; and when the ammonia is evaporated, some phosphine escapes, and there remains a complex substance.

F. A. Kekulé obtained **phosphorus pentasulphide,** P_2S_5—that is, **phosphorus tetritadecasulphide,** P_4S_{10}—by melting phosphorus and sulphur in the correct proportions. A. Stock and K. Thiel said that the product so obtained is always contaminated with some lower sulphides, so that the commercial product is really a mixture. V. and C. Meyer, H. Goldschmidt, and A. Helff obtained this sulphide from its elements. H. Rebs melted a mixture of red phosphorus and sulphur in the correct proportions; digested the product with carbon disulphide in a sealed tube; and, on cooling the soln., obtained crystals of this compound. A. Stock and B. Herscovici heated a mixture of red phosphorus and sulphur in theoretical proportions, but with one per cent. excess sulphur in an atm. of carbon dioxide. The temp. is gradually raised, and near 100°, after the reaction has spread through the whole mass, the temp., the contents begin to distil. The finely powdered product is heated in an evacuated sealed tube for several hours at 700°, and the resulting mass recrystallized several times from carbon disulphide. The crystals are finally dried at 100° in a current of hydrogen. A. Stock and W. Scharfenberg also prepared this sulphide from its elements. G. Ramme heated a carbon disulphide soln. of phosphorus and sulphur in a sealed tube for 8–10 hrs. at 210°, and recrystallized the product from its soln. in carbon disulphide in a sealed tube. E. Dervin, A. Stock, A. Stock and H. von Schönthan, and A. Stock and K. Thiel used modifications of this mode of preparation. F. Isambert obtained this sulphide by the action of sunlight on a soln. of sulphur and phosphorus in carbon disulphide. J. J. Berzelius obtained it by melting a mixture of phosphorus hemisulphide or manganese phosphodisulphide, and sulphur; or by heating molten phosphorus hemisulphide in a current of hydrogen chloride, and distilled the resulting product; A. Pauli, by the action of dry hydrogen sulphide on phospham at a red-heat; A. Besson, by the action of hydrogen sulphide on phosphoryl chloride, or of hydrogen iodide on warm thiophosphoryl sulphide; and also by heating phosphorus dioxytrisulphide in vacuo at 150°; A. Stock, by the spontaneous decomposition of dithiopyrophosphoric acid: $4H_4P_2O_2S_5 = 3P_2S_5 + 2H_3PO_4 + 5H_2S$. E. Baudrimont, by passing the vapour of thiophosphoryl chloride through a red-hot tube; A. Stock, by leaving a soln. of phosphoryl bromide in liquid hydrogen sulphide for a long time in contact with phosphorus pentoxide; and evaporating the liquid. There remains phosphorus tetritadecaphosphide. According to A. Stock, when ammonium trithiophosphate is treated with liquid hydrogen sulphide, and washed with carbon disulphide, it furnishes phosphorus tetritadecasulphide.

Analyses were made by V. and C. Meyer, A. Besson, H. Goldschmidt, A. Stock and co-workers. The results agree with the formula P_2S_5. The vap. density by V. and C. Meyer, A. Helff, and F. Isambert agrees closely with 7·67 required for P_2S_5, but W. A. Tilden and R. E. Barnett add that the low value is due to the dissociation of the molecule. A. Stock and H. von Bezold found the mol. wt. by the vap. density method decreases rapidly with rise of temp., being 208 at 600°; 196 at 650°, 185 at 700°; 144 at 800°; 136 at 900°; and 133 at 1000°. A. Stock and W. Scharfenberg made analogous observations. The mol. wt. calculated from the rise in the b.p. of carbon disulphide by the dissolved sulphide is in agreement with the formula P_4S_{10}. A. Stock and W. Scharfenberg said that the commercial sulphide is not a chemical individual and has a m.p. 255°; when recrystallized from carbon disulphide it has 3 per cent. less sulphur than is needed for P_4S_{10}. According to A. Stock and K. Thiel, the pale yellow crystalline tetritadecasulphide exists in two forms. One—the ordinary—form is sparingly soluble in carbon disulphide, and the other form is readily soluble. At 240°, the ordinary form is orange, the other yellow; the ordinary form shows no signs of melting at 273°, but begins to melt at 275°–276°, and forms a clear liquid at 279°; the other form sinters a little at 247°, is nearly all melted, and forms a clear liquid at 276°. The ordinary form is obtained by repeated crystallization from hot carbon disulphide; the other form is obtained by the rapid condensation of the vapour of the ordinary sulphide, extracting the mass with cold carbon disulphide and crystallization from the resulting soln. The ordinary sulphide gives pale yellow crystals which are fairly stable in air, the other form is nearly white, and gives off hydrogen sulphide in air. The two forms cannot be separated by fractional crystallization from carbon disulphide. The form which is more readily soluble in carbon disulphide does not exhibit a sharp m.p. While ebullioscopic determinations of the mol. wt. of the ordinary form in carbon disulphide show it to have the formula P_4S_{10}, similar determinations with the form which is more readily soluble in carbon disulphide, do not agree with the formula P_4S_{10}; the mol. wt. being smaller than that in accordance with this formula, the product is probably a mixture. The sp. gr. of the ordinary form is 2·03, that of the other form is 2·08. V. and C. Meyer, and A. Helff gave 274°–276° for the m.p.; A. Stock, 275°–276°—*vide supra.* A. Stock and B. Herscovici found the m.p. of the sulphide crystallized 10 times from carbon disulphide is 284°–291°, and there is no appreciable difference in the m.p. of the sulphide kept in vacuo for 3 months. A. Stock said that there is a partial decomposition on melting. J. J. Berzelius said that this sulphide boils at a higher temp. than sulphur, and that the vapour is paler in colour than that of sulphur. J. Mai found that the sulphide distils at 332°–340° under 10–11 mm. press., forming a pale greenish-yellow vapour. W. Hittorf gave 530° for the b.p.; H. Goldschmidt, 518° at 728·5–734 mm.; F. Isambert, 520°; M. von Recklinghausen, 523·6°; and A. Stock and B. Herscovici, 513°–515° at 760 mm. with partial decomposition; the decomposition, added A. Stock and B. Herscovici, occurs under all circumstances at 530° in a current of carbon dioxide, or in vacuo. C. Graebe, and W. Knecht recommended the use of this sulphide for the vapour-bath in vap. density determinations. R. Robl observed no fluorescence when the pentasulphide is exposed to ultra-violet light.

J. J. Berzelius found that phosphorus tetritadecasulphide burns when heated in **air** giving the characteristic phosphorus flame; while in moist air, it decomposes as readily as the tetritahexasulphide, forming phosphoric acid. F. A. Kekulé represented the decomposition by **water**: $P_2S_5+8H_2O=2H_3PO_4+5H_2S$; and A. Stock and B. Herscovici added that water attacks this sulphide slowly at ordinary temp., and rapidly when heated. L. Carius found that when a mixture of this sulphide and **thionyl chloride** is heated at 150° in a sealed tube it forms sulphur monochloride and phosphorus pentoxide, and H. Prinz represented the reaction: $6SOCl_2+2P_2S_5=4PSCl_3+3SO_2+9S$. R. F. Hunter was unable to brominate phosphorus pentasulphide by treating the soln. in chloroform or carbon disulphide with **bromine**; and a similar result was obtained with **iodine.** J. J. Berzelius said that this sulphide dissolves in aq. **ammonia** in the same manner as a deliquescent salt dissolves in water. A. Stock and B. Hoffmann found that ammonia unites additively with the sulphide, forming phosphorus dodecamminotetritadecasulphide, $P_4S_{10}.12NH_3$; and A. Stock obtained the same product by adding the sulphide to liquid ammonia. This compound is represented as *ammonium diimidopentathiopyrophosphate,* $S\{P(SNH_4)_2(NH)\}_2$; and the corresponding *diimidopentathiopyrophosphoric acid,* $P_2S_5N_2H_6$, or $P_4S_{10}.4NH_3$, *phosphorus tetramminotetritadecasulphide,* has been obtained in an impure form—*vide* phosphorus nitride. E. Glatzel obtained thiophosphoric nitrile, NPS, by the action of **ammonium chloride** on phosphorus tetritadecasulphide. E. Dervin obtained phosphorus tritahexa- and octitahena-sulphides by the fusing of a mixture of this sulphide with **phosphorus tetritatrisulphide** in the presence of carbon disulphide at 180°; R. Weber represented the reaction with **phosphorus pentachloride**: $P_2S_5+3PCl_5=5PSCl_3$; L. Carius, with **phosphoryl chloride**: $P_2S_5+5POCl_3=P_2O_5+5PSCl_3$; and E. Glatzel, with **antimony trichloride**: $P_2S_5+SbCl_3=SbPS_4+PSCl_3$. F. A. Kekulé, and L. Carius observed that the products of the reaction with **alcohol** are mercaptan, ethyl thiophosphates, and hydrogen sulphide; F. A. Kekulé, that **acetic acid** is converted into thioacetic acid; and F. D. Dodge, **acetoxime** into ammonium thiophosphate. T. E. Thorpe observed no reaction with **carbon tetrachloride** at a high temp. H. Rebs found that the tetritadecasulphide dissolves in **carbon disulphide.** A. Stock and B. Herscovici found that at room temp., say 15°, 100 parts of the solvent dissolve 0·222 part of sulphide; at 0°, 0·182 part; and at −20°, 0·0833 part; and A. Stock and K. Thiel found that 100 parts of carbon disulphide dissolve 0·513 part of the ordinary sulphide under conditions where 2·86 parts of the other variety are dissolved. C. Böttinger studied the action of the tetritadecasulphide on **organic acids**; A. Knop, on **aniline**; F. Schwarze, on **phenol**; R. Ciusa, on **benzophenonoxime**; and A. Andreocci, on **antipyrine.**

C. Friedel found that when phosphorus tetritadecasulphide is heated with **metals** on a sealed tube at a red-heat, thiohypophosphates are formed—*vide infra.* According to J. J. Berzelius, the tetritadecasulphide dissolves in a soln. of **alkali hydroxide** much as a deliquescent salt dissolves in water. The soln. has a pale yellow colour, and acids precipitate sulphur with the evolution of hydrogen sulphide. The alkali thiophosphate cannot exist in contact with water. A. Stock and B. Herscovici said that the speed of dissolution in cold soda-lye is slow, and rapid in the hot lye. C. Kubierschky observed that some mono-, di-, and tri-thiophosphates are formed—*vide infra.* J. J. Berzelius found that a cold soln. of an **alkali carbonate** slowly dissolves the tetritadecasulphide with the separation of sulphur, at about 60°. The process of dissolution is violent, no sulphur separates, but carbon dioxide is evolved. When the soln. is boiled, both carbon dioxide and hydrogen sulphide are evolved. J. J. Berzelius, and E. Glatzel observed the formation of complex sulphides by the action of the tetritadecasulphide on **metal sulphides.** L. Ferrand obtained thiohypophosphates and thiophosphate by the action of the tetritadecasulphide at 400° on metal sulphides. E. Glatzel found that **sodium monosulphide** reacts, forming the thiophosphate—*vide infra.* T. E. Thorpe and J. W. Rodger showed that **lead fluoride** or **bismuth fluoride** furnishes thiophosphoryl fluoride; E. Glatzel, that **metal chlorides** form normal thiophosphates; and that **ferric chloride** reacts: $6FeCl_3+P_4S_{10}=3FeCl_2+3FeS_2+4PSCl_3$.

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§ 38. Matches

The oldest method of procuring a flame, and one still practised by remote primitive tribes, is by dexterously rubbing together two pieces of dry wood until—in a few minutes—a few glowing particles are produced; these are quickly fanned so as to inflame dry leaves or dried decaying vegetable matters. At a later period, a stream of sparks obtained by striking a piece of steel was directed into dry *tinder*—charred linen—or dried vegetable matter. The sparks soon started the tinder glowing, and this, in contact with some inflammable substance, was fanned into a flame. In the first century of our era, Pliny, in his *Historia naturalis* (**35.** 50), said that dry wood and candles are kindled with sulphurized lamp-wicks. "Fire is struck with flint and steel; and the sulphur seizes the flame, almost sooner than it can be named. The sulphurized lamp-wicks consist either of hempen or tow cords, or small pieces of wood covered with sulphur." Several Latin writers, contemporaneous with Pliny, referred to these sulphurized lamp-wicks—*e.g.* Martial, *Epigrammata* (**1.** 42; **10.** 3), and Juvenal, *Satiræ* (**5.** 46–47)—where the Latin *sulfurata* is sometimes wrongly translated "matches" or "brimstone matches." G. Agricola [1] quoted Pliny's remarks on this subject. In 1604, M. Sandivogius wrote:

> The alchymist also being awakened out of his dream found nothing in his hand but matches which he made of brimstone so that the miserable alchymist learned nothing else by that vision but how to make matches.

The tinder box, with its accompanying flint and steel, was much used up to about 1830, and it was recently revived in the form of lighters made from auer-metal—**5.** 38, 10. Among the early devices for quickly procuring fire were the *pyrophorus powder*, free from phosphorus, which when sprinkled in air became red-hot—*e.g.* the powder obtained by roasting alum with flour, honey, or sugar out of contact with air and hermetically sealed in a glass tube; and the powder obtained by igniting Prussian blue was treated in a similar way. The *pneumatic tinder box*, and *light syringe* of R. Lorenz,[2] contained tinder which was ignited by the heat generated when air was suddenly compressed by a piston. In the *hydropneumatic lamps* or *electropneumatic fire-producers* of H. J. Mayer, and A. Fyfe, hydrogen was kindled by an electric spark; and the various modifications—by W. Eisenlohr, C. H. L. von Babo, S. von Römer, R. Hare, C. H. Pfaff, C. F. Mohr, W. Herapath,

J. Palkl, I. G. R. Schiele, and R. Böttger—of J. W. Döbereiner's *platinum lamp*, in which hydrogen gas is ignited by causing it to impinge on spongy platinum or iridium.

Many attempts were made about the end of the eighteenth century to produce fire conveniently by means of phosphorus. Thus, a particle of phosphorus was rubbed between folds of brown paper, and the resulting flame was used to ignite a splinter of wood tipped with sulphur. This was found to be inconvenient and dangerous. The so-called *phosphoric tapers*, used about 1781, consisted of wax-tapers with their wicks coated with phosphorus. They were enclosed in sealed glass tubes. To obtain a flame, the glass tube was first warmed, then broken, and the phosphorus on the taper, on exposure to air, rapidly oxidized and ignited the taper. The so-called *phosphorus bottles* or *phosphorus boxes—pocket luminaries*, and *portable fire boxes*—used 1786-1810, were internally coated with partially oxidized phosphorus. A splint of wood tipped with sulphur was introduced with the vessel so as to make a little phosphorus adhere. The oxidation of the phosphorus, assisted maybe by friction on a cork, caused the sulphur to ignite. About 1805, *oxymuriate matches*, or *chemical matches*, were made by tipping strips of wood with a mixture of potassium chlorate, sugar, and gum; they were ignited by bringing them in contact with sulphuric acid or asbestos soaked in this acid contained in a bottle. The matches were packed in boxes and sold as *Funkfeuerzeugen*, *briquets phosphoriques*, *inflammable match boxes*; *instantaneous light boxes*, *phosphorus boxes*, *eupyrion*, etc. S. Jones patented a variety which he called *promethians*. These consisted of paper tubes containing a small glass tube holding sulphuric acid coloured by indigo. The glass tube was embedded in a mixture of lycopodium, potassium chlorate, and sulphur. They were ignited by squeezing with pliers the end containing the glass tube so as to set free the acid.

About 1827, J. Walker,[3] of Stockton-on-Tees, invented the first practically useful friction matches. At first, he sold a mixture of potassium chlorate and antimony sulphide made up with gum. He called it *percussion powder*. Afterwards he dipped the tips of strips of cardboard, and then splints of wood, with the mixture, and sold these matches as *friction-lights*. They were ignited by drawing their tips between folded sandpaper held between the finger and thumb. Imitations were sold under the name *lucifers*. Some were tipped with sulphur as well as the chlorate mixture and sold as *chlorate matches*, *lucifer matches*, *allumettes infernales*, *allumettes chimiques*, and *Snellzünder*. The lucifers were followed by matches which could be ignited by friction on a suitable material fixed to the box holding the matches. The matches were tipped with a mixture of potassium chlorate, antimony sulphide, sulphur, and gum; the rubbing surface fixed on the box was coated with a mixture of potassium chlorate, red-lead, pumice-stone, and gum. Matches capable of being struck on the box came to be called *congreves*.

F. Dérosne is generally credited with having first tipped matches with a composition containing phosphorus which ignited by friction. This was about 1812; but with no marked commercial success. Between 1831 and 1833, there were several claimants for the substitution of phosphorus for antimony sulphide in the lucifer matches—*e.g.* C. Sauria of St. Lothair, France; J. F. Kammerer of Ludwigsburg, Germany; J. Irinyi, South Hungary; and J. S. Baggert of Stockholm, Sweden. There are numerous patents for modifications in the recipe—*e.g.* 1835, O. F. A. Trévani and J. Krutzler[4] recommended red-lead or manganese dioxide in place of potassium chlorate.

The manufacture of matches has been described by G. Gore,[5] W. H. Dixon, E. G. Clayton, etc. The common friction matches were made by cutting soft wood into the required shape by machinery. One end of the strip is dipped into some inflammable substance—paraffin or sulphur, and then into a paste made from yellow phosphorus, manganese dioxide, glue, and colouring matter. Other oxidizing agents can be used. The matches are then dried. The glue protects the phosphorus from oxidation, but by rubbing the head of the match on a rough surface, sufficient heat is generated to ignite the phosphorus in contact with the oxidizing agent. The burning phosphorus ignites the sulphur or paraffin, and this in turn fires the wood. Cotton threads dipped in paraffin are used in place of wood to form the so-called *wax vestas.* Numerous other suggestions have been made for the stems of matches. Various varnishes, collodion, and other preparations have been used for making the matches waterproof; and scenting ingredients—gum benzoin, frankincense, etc.—have been added to the varnishes. *Headless matches* are those in which the splint is soaked in some compound which easily gives up its oxygen. Patents for this were obtained by V. Simonet, H. Schwarz, S. Neuberg, S. L. Fog and A. G. Kirschner, C. C. Budde, G. A. Haffner, H. Huntingdon, etc.

In spite of the greatest care, the phosphorus disease was an ever-present menace in match factories using yellow phosphorus, and stringent regulations for the use of yellow phosphorus were introduced, followed by the complete prohibition of this agent in most civilized countries. The use of red phosphorus in place of yellow phosphorus was mentioned in a Swedish Government report by G. E. Pasch[6] in 1847; the process was tried in many countries, but did not succeed. The higher cost of the red phosphorus, and the unstable and dangerous nature of the mixtures employed, were largely responsible for this. Many of the advantages of the phosphorus, strike-anywhere matches were obtained by the use of phosphorus sesquisulphide, *i.e.* the tetritatrisulphide patented in 1898 by H. Sévène and E. D. Cahen; although C. Puschner, in 1860, used phosphorus sulphide in place of phosphorus. The use of scarlet phosphorus was patented by W. Muir and C. R. E. Bell in 1902; but it did not prove so efficacious as the sulphide, and it has been abandoned. Some light red phosphorus is, however, still in use in a few continental factories. Numerous other substitutes for phosphorus have been tried without success.

In 1855, R. Böttger suggested that friction matches could be made which would ignite only by friction on a specially prepared surface. The process was patented in England by F. May in 1865. The oxidizing agent—potassium chlorate, antimony sulphide, and glue—is put on the match stick, and red phosphorus, powdered glass, and glue on the box. These are the true safety matches. These matches have the disadvantage that they can be ignited only by friction on a prepared surface, or by quickly rubbing them on a smooth non-conducting surface like glass or slate; but they are not liable to ignite by accidental friction. Numerous patents have been taken for safety matches free from phosphorus—*e.g.* the oxidizing agent may be potassium chlorate, dichromate, etc., and the red phosphorus on the box was replaced by antimony oxysulphide and sulphur.

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§ 39. Phosphorus Oxysulphides; the Thiophosphoric Acids and their Salts

Compounds have been reported with part of the oxygen in phosphorus pentoxide replaced by sulphur. For example, A. Besson[1] said that **phosphorus dioxytrisulphide**, $P_2O_2S_3$, is formed when hydrogen sulphide is dissolved in phosphorus oxychloride at 0°, and the soln. is allowed to remain in a closed vessel, a yellowish-white, amorphous precipitate forms in about 24 hours, and after many weeks small, acicular crystals also separate. The amorphous product can be crystallized by dissolving it in phosphorus oxychloride in a closed vessel at 150°. When heated at 150°, the oxysulphide yields a sublimate of pentasulphide, and if heated in a vacuum at 200° for several hours, it completely decomposes into pentoxide and pentasulphide. It is slowly decomposed by water and moist air with liberation of hydrogen sulphide, burns in air or oxygen, and is violently oxidized by nitric acid.

T. E. Thorpe and A. E. H. Tutton reported **phosphorus trioxydisulphide**, $P_2O_3S_2$, to be formed when a mixture of sulphur and phosphorous oxide is heated at 160° in a sealed tube, or in an atm. of nitrogen or carbon dioxide: $P_4O_6+4S=P_4O_6S_4$. The colourless rectangular prisms are probably tetragonal terminated by a basal plane. The trioxydisulphide has a vap. density 11·8–12·5, air unity; this is in agreement with the formula required for $P_4O_6S_4$. The compound melts at about 102°, and boils without decomposition at 295°. The compound dissolves readily in twice its vol. of carbon disulphide from which soln. it can be crystallized unchanged; it also dissolves in benzene, but there is a chemical reaction with that solvent. It decomposes rapidly in air, and then smells of hydrogen sulphide, it is decomposed by water: $P_4O_6S_4+6H_2O=4HPO_3+4H_2S$.

Compounds are known in which all or part of the oxygen of the acids of phosphorus has been replaced by sulphur. Even if the parent acid is not known, salts have been obtained. Representatives of the following thiophosphorous acids have been so obtained : *monothiophosphorous acid*, $H_2(HPSO_2)$; *dithiophosphorous acid*, $H_2(HPS_2O)$; and *trithiohydrophosphorous acid*, $H_2(HPS_3)$, in which all three hydrogen atoms are replaced by a metal salt of *thiopyrophosphorous acid*, $H_4P_2S_5$, have also been reported. Representatives of *hypothiophosphoric acid*, $H_4P_2S_6$, have been obtained, as well as of *monothiophosphoric acid*, H_3PSO_3 ; of *dithiophosphoric acid*, $H_3PS_2O_2$; of *trithiophosphoric acid*, H_3PS_3O ; of *tetrathiophosphoric acid*, or *orthothiophosphoric acid*, H_3PS_4 ; of *thiopyrophosphoric acid*, $H_4P_2S_7$; of *pentathiopyrophosphoric acid*, $H_4P_2S_5O_2$; and of *trithiopyrophosphoric acid*, $H_4P_2S_3O_4$.

L. Ferrand [2] prepared a series of **thiophosphites** by heating the metals with the calculated proportions of red phosphorus and sulphur in sealed tubes. These compounds are represented as derivatives of **thiophosphorous acid,** H_3PS_3. L. Ferrand was unable to prepare *cupric thiophosphite*, $Cu_3(PS_3)_2$, in this way because the products were sulphur, phosphorus tetritahexasulphide, and cupric thiophosphate ; but he did obtain **cuprous thiophosphite,** Cu_3PS_3, by heating at 450°, in an atm. of carbon dioxide to constant weight, a mixture of 3 parts of cuprous sulphide and 4 of phosphorus pentasulphide ; and also by heating, in the absence of air and at a red-heat for 20–24 hrs., a mixture of cupric sulphide and red phosphorus ; or a mixture of copper, phosphorus, and sulphur. The orange powder may have a metallic lustre, and it consists of octahedral crystals. It decomposes at a red-heat in an inert gas, and it forms cupric oxide when heated in air. It is not attacked by water, boiling soda-lye, or boiling conc. hydrochloric acid ; fuming nitric acid decomposes it slowly in the cold ; ordinary nitric acid, and aqua regia attack it vigorously ; and with hot sulphuric acid it forms sulphur dioxide. L. Ferrand obtained a black mass of **silver thiophosphite,** Ag_3PS_3, by heating a mixture of eq. quantities of the constituent elements. The black mass is very resistant towards acids ; he obtained a similar product, Ag_4PS_3, in an analogous manner. By heating a mixture of the component elements, pale yellow, hexagonal crystals of zinc thiophosphate, $Zn_3(PS_3)_2$, can be obtained; the salt is rapidly decomposed by moist air, and by acids. L. Ferrand did not make *mercurous thiophosphite*, Hg_3PS_3, but he obtained **mercuric thiophosphite,** $Hg_3(PS_3)_2$, from the component elements at a red-heat. E. Baudrimont obtained it from a mixture of phosphorus tetritahexasulphide and mercuric sulphide. According to L. Ferrand, the orange-red crystalline mass cannot be sublimed, but it melts in vacuo without decomposition; on the other hand, E. Baudrimont said that it can be sublimed with partial decomposition ; and that when heated the salt becomes black, and red on cooling. L. Ferrand found the salt is attacked by moist air ; and is scarcely affected by cold nitric acid, but decomposed completely by the hot acid. Long, white crystals of **aluminium thiophosphite,** $Al_3(PS_3)_2$, or perhaps $AlPS_3$, are obtained by heating a mixture of the component elements. The salt is very unstable in air, and is decomposed by water and acids with the evolution of hydrogen sulphide. A black powder of **chromium thiophosphite,** $Cr_3(PS_3)_2$, was obtained in a similar manner. It consists of small hexagonal crystals with a metallic lustre. The salt is stable in moist air ; is easily attacked by hot, conc. nitric acid, and by aqua regia ; and is decomposed by fusion with a mixture of potassium hydroxide and chlorate, or by boiling with soda-lye. A black, crystalline mass of small plates of **ferrous thiophosphite,** $Fe_3(PS_3)_2$, was obtained in a similar way ; it is stable in moist air. A dark brown mass of **nickel thiophosphite,** $Ni_3(PS_3)_2$, was obtained from its component elements. It is decomposed in a few hours by moist air ; and is attacked by hot water, nitric acid, and by aqua regia.

G. Lemoine found that phosphorus tetritatrisulphide is rapidly decomposed by a soln. of sodium hydroxide with the evolution of hydrogen mixed with phosphine, and the separation of a small quantity of free phosphorus. The evaporation of the soln. in vacuo yields crystals of **sodium monothiohydrophosphite,** $Na_2(HPSO_2).2$ or $2\frac{1}{2}H_2O$.

Again, when a dil. soln. of sodium hydroxide and an excess of tetritatrisulphide, at 0°, is evaporated in vacuo, hydrogen sulphide is evolved and sodium hydrophosphite is alone deposited; if the sodium hydroxide be in excess, and the filtered soln. is left over sulphuric acid and phosphorus pentoxide for about 5 months, prismatic crystals of sodium sulphide, $Na_2S.5H_2O$, are deposited; about a month later, crystals of the monothiohydrophosphite appear; and after 4 months, crystals of **sodium monothiophosphite,** $Na_3(PSO_2).2H_2O$, are formed in which all three hydrogen atoms of the monothiophosphorous acid have been replaced by a base—a mixed sodium monothio- and dithio-phosphite was also obtained. When the tetritatrisulphide acts on sodium hydrosulphide, hydrogen sulphide and phosphine are evolved, and the soln., on evaporation in vacuo, yields crystals of **sodium dithiohydrophosphite,** $Na_2(HPS_2O).2\frac{1}{2}H_2O$.

When an excess of phosphorus tetritatrisulphide is gradually added in small portions at a time to ammonium hydrosulphide at 0°, and the liquid allowed to stand for about 15 days, crystals of ammonium hydrophosphite are formed, along with small quantities of a sulphur compound. If the mother-liquor be evaporated in vacuo, hydrogen sulphide is copiously evolved, and in about 6 or 7 months, crystals of **ammonium monothiohydrophosphite,** $(NH_4)_2(HPSO_2).H_2O$, are deposited. When this salt is dissolved in water, and the soln. evaporated in vacuo, partial hydrolysis occurs, and what is probably a mixture of thiohydrophosphite and hydrophosphite, $2(NH_4)_2O.P_2O_2S.6H_2O$, separates out. The ammonium thiohydrophosphites may also have some hydrogen sulphide in place of water of crystallization. All these salts are of the same type; sulphur replaces oxygen in phosphorous acid; and in some of them the water of crystallization, and even the water of constitution of the phosphorous acid, has been replaced by hydrogen sulphide. In the latter case, the salts lose hydrogen sulphide at ordinary temperatures. All the compounds give precipitates with most of the metallic salts. With lead acetate, they give a precipitate of the corresponding **lead thiohydrophosphite,** which has a colour varying from yellow to red. It soon decomposes into lead sulphide and phosphorous acid. With hydrochloric acid, the solid compounds give off hydrogen sulphide. When heated to 200°–240°, they lose hydrogen sulphide, but retain a portion of their sulphur, even after prolonged ignition. When their aqueous solutions are boiled, all the sulphur is given off as hydrogen sulphide, an alkaline phosphite being formed. The existence of these compounds affords further proof of the analogy between oxygen and sulphur.

J. J. Berzelius[3] reported **silver thiopyrophosphite,** $Ag_4P_2S_5$, to be formed by heating a mixture of finely divided silver, phosphorus, and sulphur in an atm. of hydrogen. There is a vigorous reaction, and much phosphorus is vaporized. The grey mass forms a pale yellow powder. The salt readily dissolves in nitric acid without the separation of sulphur.

C. Friedel[4] prepared a series of **thiohypophosphates** by heating to redness a mixture of the metal, phosphorus, and sulphur in a sealed tube. L. Ferrand also obtained some of those salts in a similar way, and also by heating to 400° a mixture of the metal sulphide with an excess of phosphorus tetritahexasulphide or tetritadecasulphide. The result with copper in both cases is to produce **copper thiohypophosphate,** $Cu_2P_2S_6$. The yellowish-brown powder contains some needle-like crystals. C. Friedel obtained **silver thiohypophosphate,** $Ag_4P_2S_6$, in a similar way; and also a pale yellow mass of **zinc thiohypophosphate,** $Zn_2P_2S_6$, consisting of pale yellow hexagonal plates of sp. gr. 2·2. The salt is insoluble in water, but is decomposed by boiling water with the evolution of hydrogen sulphide; it is not attacked by hydrochloric or nitric acid, but is decomposed by aqua regia. L. Ferrand said that it is attacked by acetic acid with the separation of sulphur. A mass of orange-yellow crystals of **cadmium thiohypophosphate,** $Cd_2P_2S_6$, was obtained by L. Ferrand by heating a mixture of the component elements at a red-heat. The salt is stable in dry air, but is decomposed by moist air, and by cold nitric acid. C. Friedel prepared a sulphur-yellow crystalline mass of **mercuric**

thiohypophosphate, $Hg_2P_2S_6$, from a mixture of the elements heated in a sealed glass tube. The salt gradually blackens when exposed to light; and in the presence of an excess of phosphorus sulphide it can be sublimed; but it is decomposed when heated alone. The salt is slowly decomposed by boiling water with the evolution of hydrogen sulphide; it is rapidly attacked by potash-lye with the separation of mercuric sulphide. C. Friedel made brownish-white **aluminium thiohypophosphate,** $Al_4(P_2O_6)_3$, by heating a mixture of the constituent elements in a sealed tube. The white crystal plates are transparent; they rapidly become matte when exposed to air, and are decomposed by water with the evolution of hydrogen sulphide. C. Friedel made **stannic thiohypophosphate,** SnP_2S_6, by the same method; **stannous thiohypophosphate,** $Sn_2P_2S_6$, seems to be formed in a similar way using the right proportions of the three elements. The yellowish-brown mass of either salt is decomposed by boiling water with the evolution of hydrogen sulphide. C. Friedel, and L. Ferrand prepared **lead thiohypophosphate,** $Pb_2P_2S_6$, by the methods indicated above. The orange-yellow crystalline mass is not attacked by water. L. Ferrand reported **chromium thiohypophosphate,** $Cr_2P_2S_6$, to be formed by heating a mixture of the component elements to redness for 24 hrs. The black powder consists of hexagonal plates; it is insoluble in nitric acid; almost insoluble in aqua regia; and attacked by molten sodium carbonate. C. Friedel prepared **iron thiohypophosphate,** $Fe_2P_2S_6$, in a similar way. It forms brilliant, greyish-black, hexagonal lamellæ resembling those of graphite or specular hæmatite. The lamellæ, when very thin, are brown by transmitted light, and have no action on parallel polarized light. The compound is attacked by nitric acid, but more easily by a mixture of the acid with potassium chlorate. L. Ferrand prepared **nickel thiohypophosphate,** $Ni_2P_2S_6$, by heating a mixture of the component elements to redness for 14 hrs. It forms brilliant, grey, hexagonal crystals of sp. gr. 2·4. It is stable towards moist air, and is not affected by water or cold acids; aqua regia attacks it slowly; it is decomposed by a mixture of nitric acid and potassium chlorate.

L. Ferrand[5] prepared some normal **thio-orthophosphates** by the action of phosphorus tetritahexasulphide, or tetritadecasulphide on the metal sulphide at 400°; and E. Glatzel, by heating phosphorus tetritadecasulphide with the metal chloride: $3MCl_2+P_2S_5=PSCl_3+M_3PS_4+3Cl$; or sulphide: $3M_2S+P_2S_5=2M_3PS_4$. All these thiophosphates burn with a livid flame when heated in air; they are all insoluble in water, alcohol, ether, benzene, carbon disulphide, and acetic acid; some are decomposed by sulphuric or hydrochloric acid with the evolution of hydrogen sulphide; but they are not affected by aq. ammonia, or potash-lye; boiling nitric acid, aqua regia, or nitric acid and bromine easily decomposes these salts; and they yield sulphur dioxide when heated with conc. sulphuric acid. According to F. Ephraim and E. Majler, when sodium thiophosphate, Na_3PS_4, is treated with the solutions of sulphides of other metals, reaction takes place either according to the equation: $2Na_3PS_4+3M_2S+2H_2O=2M_3PS_3O+3Na_2S+2H_2S$, or according to the equation: $2Na_3PS_4+3M_2S+4H_2O=2M_3PS_2O_2+3Na_2S+4H_2S$. In no case is the tetrathiophosphate of the second metal formed, owing to hydrolysis by the water.

E. Glatzel was unable to make normal **ammonium thiophosphate,** $(NH_4)_3PS_4$, by heating phosphorus sulphide with ammonium chloride; nor did he obtain the normal **sodium thiophosphate,** Na_3PS_4, by heating a mixture of a mol of phosphorus sulphide with 3 mols of sodium chloride; but he did obtain **octohydrated sodium thiophosphate,** $Na_3PS_4.8H_2O$, by fusing sodium monosulphide and phosphorus tetritadecasulphide: $3(Na_2S.9H_2O)+P_2S_5=2(Na_3PS_4.8H_2O)+11H_2O$. A conc. aq. soln. of the product deposits crystals of the salt. The salt cannot be recrystallized from water without decomposition. The pale yellow or colourless crystals, acicular or tabular, belong to the monoclinic system. When heated, the salt decomposes with the loss of the water of crystallization; acids decompose the salt with the evolution of hydrogen sulphide; with conc. sulphuric acid or conc. nitric acid, there is a separation of sulphur; with soln. of the metal salts, coloured precipitates or coloured soln. are obtained. He obtained **potassium thiophosphate,** K_3PS_4, contaminated with some phosphorus tetritadecasulphide, and potassium chloride. The yellow salt is fusible, and freezes to a crystalline mass. It dissolves in water or dil. acid with the evolution of hydrogen sulphide; but dissolves in aq. ammonia or potash-lye without developing a gas.

E. Glatzel made **cuprous thiophosphate,** Cu_3PS_4, from cuprous chloride and the vapour of phosphorus sulphide; and L. Ferrand, by treating copper sulphophosphides with the vapour of phosphorus sulphide; by the action of phosphorus tetritadecasulphide on cuprous sulphide; by heating cuprous sulphide, phosphorus, and sulphur to redness; by heating cuprous thiophosphite in vacuo, and washing the product with carbon disulphide, alcohol, and finally with ether; and also by heating a mixture of the elements to redness. The yellowish-brown or reddish-yellow powder consists of microscopic crystals, which burn when heated in air. The salt is decomposed by boiling nitric or sulphuric acid, aqua regia, or a mixture of nitric acid and bromine; but is not affected by aq. ammonia, or alkali-lye. Attempts to make **cupric thiophosphate,** $Cu_3(PS_4)_2$, always gave the cuprous salt. E. Glatzel prepared **silver thiophosphate,** Ag_3PS_4, from silver chloride and phosphorus tetritadecasulphide. The sulphur-yellow crystalline mass readily fuses to an orange-red or greyish-black mass, which when triturated gives a yellow powder. It is blackened when treated with alkali-lye. It is insoluble in water, organic solvents, and in acetic, hydrochloric, dil. sulphuric, and nitric acids, but it gives off sulphur dioxide when heated with conc. sulphuric acid, and yields silver chloride when treated with aqua regia.

Attempts to make **calcium, strontium, and barium thiophosphates** by the general methods were not successful. E. Glatzel obtained **zinc thiophosphate,** $Zn_3(PS_4)_2$, from the dry chloride and phosphorus tetritadecasulphide. The small, colourless, or white crystal plates burn with a livid flame in air without melting. The salt is decomposed by nitric acid and bromine, and by aqua regia; it is insoluble in water, aq. ammonia, and alkali-lye. Small white plates of the corresponding **cadmium thiophosphate,** $Cd_3(PS_4)_2$, was prepared in a similar manner, and its properties were similar to those of the zinc salt. Attempts to make mercurous thiophosphate, Hg_3PS_4, always yielded **mercuric thiophosphate,** $Hg_3(PS_4)_2$, which is best obtained from mercuric sulphide and phosphorus tetritadecasulphide. The red crystalline mass looks like potassium dichromate; it burns with a livid flame, without melting. It is insoluble in water, organic solvents, aq. ammonia, and in acetic, hydrochloric, nitric, and dil. sulphuric acids. Conc. nitric acid, and aqua regia have no action; hot conc. sulphuric acid gives sulphur dioxide; it is readily dissolved by a mixture of nitric acid and bromine; and is blackened by potash-lye.

E. Glatzel prepared **thallous thiophosphate,** Tl_3PS_4, by a method analogous to that used for the mercuric salt. The yellow crystalline mass melts and burns with a green flame; it is insoluble in water, organic solvents, and acetic acid; it is decomposed when heated with dil. sulphuric or hydrochloric acid; it dissolves in warm nitric acid, and in aqua regia; it gives sulphur dioxide when heated with conc. sulphuric acid; it is not attacked by aq. ammonia; and blackens when treated with alkali-lye. E. Glatzel obtained **stannous thiophosphate,** $Sn_3(PS_4)_2$, by the reaction: $3SnCl_2+2P_2S_5=2PSCl_3+Sn_3(PS_4)_2$, as a grey, crystalline mass, which burns in air. It is insoluble in water, organic solvents, and acetic, dil. hydrochloric and sulphuric acids; when heated with conc. sulphuric acid it gives sulphur dioxide; and it is decomposed by nitric acid and bromine, aqua regia, alkali-lye, and aq. ammonia. Attempts to make **stannic thiophosphate,** $Sn_3(PS_4)_4$, were nugatory. A grey crystalline mass of **lead thiophosphate,** $Pb_3(PS_4)_2$, was prepared by the method employed for the stannous salt. Its properties are similar.

E. Glatzel obtained a grey, crystalline mass of **arsenic thiophosphate,** $AsPS_4$, by heating a mixture of arsenic trisulphide and phosphorus tetritadecasulphide.

The salt melts easily and can be distilled without decomposition; it burns with a livid flame when heated in air; it is insoluble in water and organic solvents; hydrochloric acid has no action; dil. sulphuric acid decomposes it with the evolution of hydrogen sulphide, and when heated with conc. sulphuric acid, it yields sulphur dioxide. It is dissolved by nitric acid, aq. ammonia, and alkali-lye. E. Glatzel prepared **antimony thiophosphate,** $SbPS_4$, by the action of phosphorus tetritadecasulphide on antimony trisulphide or trichloride. Forty grms. of the finely-powdered phosphorus sulphide are mixed with 80 grms. of antimony trichloride by shaking in a retort, and warmed for one hour on the sand-bath with the neck of the retort pointing upwards; when the reaction is ended, the phosphorus thiochloride and excess of antimony trichloride are distilled off. The antimony thiophosphate which remains in the retort is bright yellow; it melts when the temp. is raised, and solidifies on cooling in radiating, fibrous crystals of brilliant, silky lustre; when ground up, it yields a straw-coloured felted mass which smells of hydrogen sulphide, is insoluble in water, alcohol, ether, carbon bisulphide, hydrochloric acid, dil. sulphuric acid, benzene, and acetic acid, but is decomposed when boiled with conc. nitric acid, aqua regia, conc. sulphuric acid, and soln. of potassium or sodium hydroxide, and burns with a pale flame when heated in the air. When heated at its m.p. for some time, decomposition takes place, a part of the phosphorus sulphide distils off, and a ruby-red, amorphous mass remains. E. Glatzel made **bismuth thiophosphate,** $BiPS_4$, from the chloride: $BiCl_3+P_2S_5=BiPS_4+PSCl_3$. The dark grey, crystalline mass burns with a livid flame when heated in air; it is insoluble in water, and in organic solvents. It is decomposed by boiling hydrochloric acid with the evolution of hydrogen sulphide; hot conc. sulphuric acid gives sulphur dioxide; dil. sulphuric acid has no action; nitric acid and aqua regia decompose it with the separation of sulphur; and it is decomposed by aq. ammonia, and alkali-lye.

E. Glatzel prepared **manganese thiophosphate,** $Mn_3(PS_4)_2$, from manganese sulphide and phosphorus tetradecasulphide. The greenish plates burn with a yellowish-white flame, without melting when heated in air. When heated to a high temp., phosphorus sulphide distils off, leaving manganese sulphide. The salt is insoluble in water, and in organic solvents; it is not attacked by hydrochloric acid, it is easily decomposed by nitric acid, and by aqua regia with the separation of sulphur; dil. sulphuric acid is without action; and hot, conc. sulphuric acid furnishes sulphur dioxide. Attempts to make **ferric thiophosphate** were a failure because the reaction proceeds: $3Fe_2Cl_6+2P_2S_5=3FeCl_2+3FeS_2+4PSCl_3$, and not $2FeCl_3+2P_2S_5=2PSCl_3+Fe_2(PS_4)_2$. E. Glatzel obtained **ferrous thiophosphate,** $Fe_3(PS_4)_2$, from ferrous sulphide, not the chloride. The black crystalline plates burn in air with a livid flame, without melting. The salt is insoluble in water, organic solvents, and in acetic, dil. sulphuric and hydrochloric acids; it is decomposed by nitric acid, and aqua regia; and it is decomposed by hot, conc. sulphuric acid with the evolution of sulphur dioxide. Aq. ammonia, and alkali-lye have no action. E. Glatzel obtained **nickel thiophosphate,** $Ni_3(PS_4)_2$, by the reaction: $3NiCl_2+2P_2S_5=Ni_3(PS_4)_2+2PSCl_3$. The dark brown, crystalline plates burn in air without melting, and are decomposed at a high temp. giving off phosphorus sulphide and leaving a residue of nickel sulphide. The salt is insoluble in water, organic solvents, and acetic, hydrochloric, and dil. sulphuric acids; it is decomposed by nitric acid, aqua regia, and hot conc. sulphuric acid. Warm aq. ammonia, or alkali-lye gave a green or brown coloration.

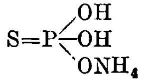
C. Kubierschky[6] prepared a series of **oxythiophosphates** with only part of the oxygen of the normal phosphates replaced by sulphur. He said that acids decompose all thiophosphates; hydrogen sulphide is evolved, and, in some cases, sulphur separates. Monothiophosphates give white precipitates with calcium, barium, and strontium salts, the dithiophosphates with barium and strontium salts, and the trithiophosphates with barium salts only. All thiophosphates yield precipitates with cadmium, copper, silver, and mercurous salts, which decompose after a time, forming the sulphides of the metals. With a dithiophosphate, manganese sulphate gives a green coloration, which becomes darker on shaking; a further addition of manganese sulphate gives a dark green precipitate, which gradually becomes white, but on shaking changes back to green. Ferrous salts give a dirty greyish-green precipitate with monothiophosphates. Ferric salts give red colorations with all thiophosphates, from which solutions, on boiling, ferrous sulphide separates out. An excess of ferric chloride gives a precipitate with monothiophosphates only, which, on continued boiling, is decomposed with the production of iron phosphate and sulphuretted hydrogen. A soln. of a thiophosphate containing a small quantity of an alkaline sulphide gives an intense green coloration with ferric chloride. Cobalt sulphate gives with a monothiophosphate a blue precipitate soluble in excess of the latter to a blue soln.; the dithiophosphates give dirty green precipitates, soluble in excess of the thiophosphate to green soln.; the trithiophosphates give a red to a brown coloration. In each case, boiling produces a precipitate of cobalt sulphide. Nickel sulphate in excess gives a light green precipitate with monothiophosphates, and a dirty blue precipitate with a dithiophosphate. Many of these coloured soln., produced as above described, exhibit characteristic absorption-spectra. Nitric acid decomposes all thiophosphates with a precipitation of sulphur; potassium permanganate, dichromate, and ferricyanide, are reduced by thiophosphates, sulphur separating out in each case. Monothiophosphates decolorize iodine soln. with an immediate precipitation of sulphur, whereas in the case of the di- and tri-thiophosphates the separation of sulphur takes place only after some time or on boiling.

According to C. Kubierschky, **trithiophosphoric acid,** H_3PS_3O, or $(HS)_3PO$, cannot be isolated from its salts because the liberated acid immediately decomposes with the separation of sulphur and the evolution of hydrogen sulphide. C. Kubierschky did not succeed in isolating **sodium trithiophosphate,** Na_3PS_3O, but a soln. of the salt is produced when phosphorus tetritadecaphosphate reacts with a soln. of sodium hydrosulphide below 20°. A. Stock, however, obtained the secondary sodium salt, **sodium hydrotrithiophosphate,** $(NaS)_2(HS)PO$, by the action of sodium ethoxide on the tertiary ammonium salt. It is easily soluble in water, and in methyl alcohol, but decomposes when heated with the evolution of hydrogen sulphide. A. Stock and co-workers prepared **ammonium trithiophosphate,** $PO(SNH_4)_3.H_2O$, by the action of water on ammonium imidotrithiophosphate; it slowly loses water in a vacuum desiccator, and the aq. soln. gives precipitates of various salts when added to soln. of the metal salts. A. Stock obtained **copper trithiophosphate** from a soln. of copper sulphate and ammonium trithiophosphate; and **silver trithiophosphate** from an ammoniacal soln. of silver nitrate. F. Ephraim and E. Majler obtained **barium trithiophosphate,** $Ba_3(PS_3O)_2.20H_2O$, from normal sodium thiophosphate and a soln. of barium sulphide. The salt is stable when dry, but is decomposed by water or dil. acids with the evolution of hydrogen sulphide. Conc. nitric acid dissolves it, oxidizing the sulphur to sulphuric acid. Unsuccessful attempts were made to prepare **strontium trithiophosphate,** and **calcium trithiophosphate**; A. Stock, however, did make the calcium salt from a soln. of the ammonium salt and a soln. of a calcium salt. F. Ephraim and E. Majler prepared **magnesium trithiophosphate,** $Mg_3(PS_3O)_2.20H_2O$, by the action of normal sodium thiophosphate on a soln. of magnesium hydrosulphide. It is precipitated by alcohol from the aq. soln. in the form of white needles. It is decomposed by water and dil. acids. A. Stock obtained white precipitates of **zinc trithiophosphate** from the ammonium salt and a soln. of zinc sulphate; **cadmium trithiophosphate** from a soln. of cadmium sulphate; **mercuric trithiophosphate** from a soln. of mercuric chloride; **lead trithiophosphate,** $Pb_3(PS_3O)_2$, from lead nitrate; **bismuth trithiophosphate** from bismuth nitrate; and **chromium trithiophosphate** from a soln. of chromium sulphate.

C. Kubierschky found that when **dithiophosphoric acid,** $H_3PS_2O_2$, is liberated from its salts, the acid immediately decomposes with the separation of sulphur and the evolution of hydrogen sulphide. C. Kubierschky prepared **ammonium dithiophosphate,** $(NH_4)_3PS_2O_2.2H_2O$, by the action of aq. ammonia on phosphorus tetritadecasulphide; the soln. gives acicular crystals which effloresce, and at the same time decompose with the separation of sulphur. A. Stock obtained it by adding alcohol to a soln. of ammonium imidotrithiophosphate until it appears turbid, then a few drops of water until the soln. clarifies, and then pour a layer of alcohol over the soln. and allow it to stand 24 hrs. This salt is also produced when normal ammonium trithiophosphate is treated with water at ordinary temp. C. Kubierschky said that the colourless needles effloresce in air and sulphur is separated. He also prepared **sodium dithiophosphate,** $Na_3PS_2O_2.11H_2O$, by dissolving in water the mixture of thiophosphates obtained by adding a mol of powdered phosphorus tetritadecasulphide to a moderately conc. soln. of 6 mols of sodium hydroxide, and heating the soln. at 50°–55°, until all trithiophosphate has been destroyed, as shown by a drop of the soln. giving a green instead of a yellow or brown coloration with a soln. of cobalt sulphate. The soln. is now cooled, as further heating converts the dithiophosphate into the monothiophosphate, and alcohol is added; a precipitate of almost pure sodium dithiophosphate is then formed which may be purified by crystallization from water. It forms colourless, six-sided crystals, melting at 45°–46°; it decomposes into monothiophosphate or phosphate and sulphur, at temperatures a little above the ordinary. The corresponding **lithium dithiophosphate,** $Li_3PS_2O_2$, is a soluble salt by the action of ammonium dithiophosphate on a lithium salt soln. **Potassium dithiophosphate,** $K_3PS_2O_2$, could be obtained only in soln. C. Kubierschky obtained precipitates of **copper dithiophosphate** by adding sodium dithiophosphate to a soln. of copper sulphate; and **silver dithiophosphate** was obtained in an analogous way. Unstable **calcium dithiophosphate,** $Ca_3(PS_2O_2)_2.nH_2O$, was obtained in needle-like crystals by the rapid evap. of the aq. soln. The aq. soln. is decomposed by alcohol. When a soln. of sodium dithiophosphate is added to one of barium chloride, **barium dithiophosphate,** $Ba_3(PS_2O_2)_2.8H_2O$, is formed as a white precipitate. F. Ephraim and E. Majler prepared barium dithiophosphate, $Ba_3(PS_2O_2)_2.18H_2O$, by the action of normal sodium thiophosphate on a soln. of barium hydrosulphide. C. Kubierschky obtained **strontium dithiophosphate,** and calcium dithiophosphate by the method employed for the barium salt. Unstable **magnesium dithiophosphate,** $Mg_3(PS_2O_2)_2.nH_2O$, was obtained by the process employed for the calcium salt. It is very soluble in water. When a soln. of sodium dithiophosphate is added to one of magnesium sulphate in the presence of ammonia, **ammonium magnesium dithiophosphate,** $MH_4MgPS_2O_2.6H_2O$, is formed. It closely resembles the magnesium salt. C. Kubierschky found that sodium dithiophosphate precipitates **mercurous dithiophosphate** from soln. of mercurous salts; an excess of the sodium salt with mercuric chloride gives when boiled a black precipitate, but with an excess of mercuric chloride, the precipitate remains white when boiled. A green soln. is obtained with manganese sulphate; greenish soln. with ferrous sulphate; red soln. with ferric salts; bluish-violet soln. with nickel sulphate; and a dirty green precipitate—**cobalt dithiophosphate**—with cobalt sulphate which with an excess of the dithiophosphate becomes bright green.

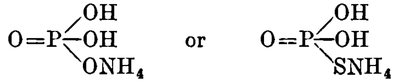
According to C. A. Wurtz, **monothio-orthophosphoric acid,** H_3PSO_3, is liberated from its salts by the feeblest of acids, but it is immediately hydrolyzed: $H_3PSO_3+H_2O=H_3PO_4+H_2S$, and, added A. Michaelis, some phosphorus acid and sulphur are formed at the same time. C. Kubierschky prepared **sodium monothiophosphate,** $Na_3PSO_3.12H_2O$, from the mixture employed for the preparation of the dithiophosphate. The soln. was treated with alcohol to precipitate the thiophosphates. The precipitated thiophosphates are dissolved in water, and the soln. heated at 90° for some time, in order to decompose the dithiophosphate into monothiophosphate and from this soln., on cooling, the latter separates out in white six-sided tablets, melting at 60°. This salt is identical with that obtained by C. A. Wurtz by the action of phosphorus thiochloride on sodium hydroxide:

$PSCl_3+6NaOH=Na_3PSO_3+3NaCl+3H_2O$. T. E. Thorpe and J. W. Rodger obtained it likewise from the thiophosphoryl fluoride. B. Rathke obtained it by C. Kubierschky's process. The hexagonal crystals were examined by F. de la Provostaye. C. Kubierschky said the crystals melt at 60°, and readily form undercooled soln. C. A. Wurtz found that the crystals dissolve readily in hot water and are deposited on cooling; the aq. soln. is alkaline. According to C. A. Wurtz, chlorine, bromine, iodine, or nitric acid reacts according to the type equation: $Na_3PSO_3+Cl_2+H_2O=NaH_2PO_4+2NaCl+S$—*vide supra*, general reactions of the thiophosphates. C. Kubierschky could obtain **potassium monothiophosphate,** K_3PSO_3, only in soln.; and similarly with normal or tertiary **ammonium monothiophosphate,** $(NH_4)_3PSO_3$. A. Stock obtained the tertiary salt by the action of aq. ammonia on the primary salt—*vide infra*. It occurs as a bone-white, crystalline powder which loses 2 mols of ammonia when gently heated or dried over sulphuric acid in vacuo. It gives precipitates with soln. of the metal salts—*vide supra*. A. Stock prepared primary ammonium monothiophosphate or **ammonium dihydromonothiophosphate** by the action of water on imidotrithiophosphoric acid: $NHP(SH)_3+3H_2O=2H_2S+PO(OH_2)(SNH_4)$. By repeated soln. in water, and precipitation with alcohol, a colourless salt is obtained. When the salt is heated it forms hydrogen sulphide and ammonium metaphosphate. It is not clear if the ammonium radicle replaces the hydrogen of an OH-group. F. D. Dodge prepared ammonium dihydromonothiophosphate, $(NH_4O)(OH)_2PS$, or $(NH_4)H_2PSO_3$, in which the sulphur is associated with the phosphorus atom:



$$\mathrm{S{=}P}\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{ONH_4}\end{matrix}$$

F. D. Dodge's salt.



$$\mathrm{O{=}P}\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{ONH_4}\end{matrix} \quad \text{or} \quad \mathrm{O{=}P}\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{SNH_4}\end{matrix}$$

A. Stock's salt.

The former is deposited in yellow crystals, mixed with sulphur; when acetoxime is treated with phosphorus pentasulphide in carbon bisulphide soln.; the insoluble product extracted with alcohol; and the alcoholic soln. heated to boiling; the compound separates from cold water in large, transparent, seemingly monoclinic prisms, melts at 146°–150° with decomposition, and is readily soluble in water, but only sparingly in alcohol, and insoluble in ether and carbon bisulphide. It decomposes carbonates, gives a colourless precipitate with lead acetate, and is decomposed by hot dilute nitric acid with separation of sulphur and formation of phosphoric acid; it is also decomposed by mercuric oxide, the filtrate from the precipitated mercury sulphide giving all the reactions of phosphoric acid.

C. A. Wurtz precipitated **copper monothiophosphate,** $Cu_3(PSO_3)_2$, from a copper salt soln. by adding sodium dithiophosphate. The salt is very unstable. He also obtained **silver monothiophosphate** in an analogous way. C. A. Wurtz, and C. Kubierschky obtained **calcium, strontium, and barium monothiophosphates** in a similar way from a soln. of a salt of the alkaline earth and sodium monothiophosphate; **magnesium monothiophosphate,** $Mg_3(PSO_3)_2.20H_2O$, was also prepared as a white crystalline precipitate on adding a soln. of the sodium salt to one of magnesium sulphate; and **ammonium magnesium monothiophosphate,** $(NH_4)MgPSO_3.9H_2O$, was obtained by a process analogous to that employed for the dithiophosphate. C. Kubierschky obtained precipitates of **cadmium monothiophosphate,** and **mercurous monothiophosphate** by adding the sodium salt to a soln. of a cadmium or mercurous salt; with a little mercuric chloride the precipitate is black; while **lead monothiophosphate** obtained in a similar way is white, but it soon becomes black by the separation of lead sulphide. Soln. of manganese sulphate give **manganese monothiophosphate**; and a ferrous salt soln. gives **ferrous monothiophosphate**; and with a ferric salt, a red soln. is obtained which decomposes with the separation of sulphur when boiled. C. A. Wurtz, and C. Kubierschky also obtained a blue precipitate of **cobalt monothiophosphate,** and green **nickel monothiophosphate,** both of which become black with boiling soln.

L. Ferrand prepared a series of thiopyrophosphates by heating the metals with the required proportions of sulphur and phosphorus in a sealed tube. In the case of **cuprous thiopyrophosphate,** $Cu_4P_2S_7$, L. Ferrand heated a mixture of the constituent elements to redness; and also a mixture of cuprous sulphide, sulphur, and phosphorus in a sealed tube at a red-heat. The blue, crystalline mass is red in transmitted light; when heated in air, it forms cupric sulphide and phosphorus pentoxide, and at a dark red-heat cuprous oxide. Hot sodium hydroxide decomposes it, forming cuprous sulphide; with hot sulphuric acid it forms sulphur dioxide; and it is not attacked by cold sulphuric acid or hot hydrochloric acid. J. J. Berzelius reported **cupric thiopyrophosphate,** $Cu_2P_2S_7$, to be formed by heating cupric diphosphodisulphide with sulphur. L. Ferrand could not confirm this. J. J. Berzelius obtained **silver thiopyrophosphate,** $Ag_4P_2S_7$, by the method he used for the cupric salt; and L. Ferrand obtained it from its elementary components. According to J. J. Berzelius, the brownish or orange-yellow mass forms silver pyrophosphite (*q.v.*). L. Ferrand found that silver thiopyrophosphate is not attacked by boiling nitric acid, but it is completely decomposed by aqua regia. L. Ferrand obtained **zinc thiopyrophosphate,** $Zn_2P_2S_7$, from its elements. The pale yellow crystals are decomposed by water, and by acetic acid. He also prepared **cadmium thiopyrophosphate,** $Cd_2P_2S_7$, as a white, crystalline powder; it is rapidly decomposed by moist air; and only slightly attacked by hot nitric acid. L. Ferrand made **mercurous thiopyrophosphate,** $Hg_4P_2S_7$, as a red, crystalline powder which decomposes in moist air, and is attacked by hot nitric acid. J. J. Berzelius obtained **mercuric thiopyrophosphate,** $Hg_2P_2S_7$, by the method he used for the cupric salt; but L. Ferrand could not make it. White, needle-like crystals of **aluminium thiopyrophosphate,** $Al_2(P_2S_7)_3$, were obtained from the constituent elements. The product is unstable in moist air, and is decomposed by water, alkali-lye, and acids. Red, octahedral crystals of **lead thiopyrophosphate,** $Pb_2P_2S_7$, were obtained. The salt is fairly stable in moist air; decomposed by water; but is not attacked by cold nitric acid. The black, hexagonal lamellæ of **chromic thiopyrophosphate,** $Cr_2(P_2S_7)_3$, is very resistant towards nitric acid and aqua regia, but is decomposed by water, and moist air. The small, lustrous lamellæ of **ferrous thiopyrophosphate,** $Fe_2P_2S_7$, are insoluble in cold nitric acid. The deep brown crystals of **nickel thiopyrophosphate,** $Ni_2P_2S_7$, are decomposed by water and moist air, and attacked by nitric acid at 150°.

According to A. Stock, when lead or ammonium trithiophosphate is treated with anhydrous liquid hydrogen chloride, a yellow oil is obtained. Its composition corresponds with that of a mixture of thiophosphoric acids, or else with **pentathiopyrophosphoric acid,** $H_4P_2O_2S_5$. The m.p. is approximately $-55°$; and, at ordinary temp. it decomposes: $4H_4P_2O_2S_5=3P_2S_5+2H_3PO_4+5H_2S$. It reacts energetically with water with the deposition of sulphur. It is soluble in carbon disulphide. It reacts with dry ammonia, forming what appears to be **ammonium pentathiopyrophosphate.** According to A. Michaelis, when thiopyrophosphoryl tetrabromide is treated with water, sulphur, hydrogen sulphide, thiophosphoryl bromide, and **trithiopyrophosphoric acid,** $H_4P_2O_4S_3$, or $(HO)_4P_2S_3$, are formed. It is thought to have the constitution $(HO)_2{=}PS{-}S{-}SPS{=}(OH)_2$; and ethyl trithiophosphate was prepared. When the aq. soln. of the acid is treated with ammonium and a magnesium salt, no precipitate is formed in the cold, but when heated, a crystalline precipitate is deposited. The precipitate is soluble in acids, and the soln. soon gives off hydrogen sulphide and deposits sulphur. The aq. soln. of the acid gives a black precipitate with silver nitrate, and with lead acetate, white **lead trithiopyrophosphate** is probably formed which blackens when the soln. is boiled.

A. Stock found that light yellow **ammonium dithiometaphosphate,** $(NH_4S)POS$, or $(NH_4O)PS_2$, is formed when dry hydrogen sulphide acts on ammonium trithiophosphate at 175°. The salt is decomposed by water with the evolution of hydrogen sulphide.

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§ 40. Phosphorus Sulphates

R. Weber[1] reported the complex $P_2O_5.3SO_3$ to be formed by the action of phosphorus pentoxide on sulphur trioxide, in the cold. It can be regarded as **phosphoryl sulphate,** $(PO)_2(SO_4)_3$, or as *sulphuryl phosphate,* $(SO_2)_3(PO_4)_2$. The white mass consists of transparent plates. It decomposes at 25°–30° with the evolution of sulphur trioxide. R. H. Adie added phosphoric acid very slowly to a cold mixture of sulphur trioxide and obtained a pale brown liquid with the composition $H_3PO_4.3SO_3$. This can be regarded as **phosphoryl hydrosulphide,** $PO(HSO_4)_3$. The compound fumes in air and is slowly decomposed by water, forming phosphoric and sulphuric acids.

C. Friedheim obtained complex salts crystallizing from aq. soln. of the components. Thus, with a mixture of $H_2SO_4 : 2NH_4(H_2PO_4)$, he obtained **ammonium sulphatophosphate,** $HO.PO(ONH_4).O.SO_2.ONH_4+H_2O$; and with the mixture $2KH_2PO_4 : H_2SO_4$, or $2H_3PO_4 : K_2SO_4$, he obtained **potassium sulphatophosphate,** $HO.PO(OK).O.SO_2.OK+H_2O$.

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§ 41. Thiophosphoryl Halides, and Phosphorus Thiohalides

T. E. Thorpe and J. W. Rodger[1] prepared **thiophosphoryl fluoride,** PSF_3, by heating phosphorus tetritadecasulphide, or a mixture of phosphorus and sulphur, with an excess of lead fluoride: $3PbF_2+P_2S_5=3PbS+2PSF_3$, in a current of dry nitrogen in a leaden tube not over 250°, and collecting the gases over mercury; bismuth fluoride gives a similar result. They also obtained it by the action of arsenic trifluoride on thiophosphoryl chloride in a sealed tube at 150°: $AsF_3+PSCl_3=PSF_3+AsCl_3$; and C. Poulenc, by the action of sulphur, or antimony trisulphide on phosphorus trifluodichloride. At ordinary temp., thiophosphoryl fluoride is a transparent, colourless gas. The analysis and vap. density were found by T. E. Thorpe and J. W. Rodger to agree with the formula PSF_3. The gas condenses to a colourless liquid at 10–11 atm. press. At 3·8°, the gas liquefies at 7·6 atm. press.; at 10° and 9·4 atm. press.; at 13·8° and 10·3 atm. press.; and at 20·3° and 13 atm. press. When a tube of the gas is exhausted while electric sparks are passing, the spectrum consists of lines characteristic of the fluorine spectrum as seen in silicon fluoride and boron fluoride. After a time, as the press. is reduced, lines of phosphorus appear and entirely displace the fluorine spectrum. On further reducing the press., the phosphorus lines give place to a spectrum consisting entirely of sulphur flutings. Thiophosphoryl fluoride is therefore dissociated at the lowest temperature of the spark. The compound is decomposed by heat, forming sulphur, phosphorus, and phosphorus fluorides. The first action is considered to be: $PSF_3=PF_3+S$, and $5PF_3=3PF_5+2P$. A similar decomposition occurs when electric sparks are passed through the gas. If the decomposition be effected in a glass tube, at a sufficiently high temp., the gaseous product eventually consists entirely of silicon tetrafluoride. If a small quantity of mercury fulminate be exploded in the gas, a black deposit of mercuric sulphide is produced in quantity sufficient to show that all the sulphur is thrown out of combination. Thiophosphoryl fluoride is quickly decomposed by **air.** If a very slow stream of the pure gas be allowed to issue from a narrow platinum jet into the air, a white fume is instantly formed. No indication of flame is evident in daylight if the stream is sufficiently slow, but in the dark, the white fume is seen to be traversed in the vicinity of the jet by a blue, flickering flame. On increasing the current of the issuing gas the blue, flickering flame becomes more pronounced, and eventually travels back to the orifice of the jet, and ignites the stream. If the supply of gas is maintained, the gas continues to burn, giving off copious white fumes. The flame is greyish-green in colour, and is tipped with a faintly luminous, dull yellow portion, a light-blue zone occurring close to the platinum jet. If, instead of allowing the gas to issue from a jet, a considerable bulk be suddenly permitted to come in contact with the air, combination rapidly takes place, accompanied first of all by a beautiful blue flash of light followed by the greyish-green flame observed in the case of a jet of the gas. The shape of the flame indicates that the gas has spread itself for a considerable way over the surface of the mercury before combination ensues. If the layer of fume be allowed to rise above the top of the tube, the gas is no longer protected from the action of the air, and takes fire from above and burns with the greyish-green flame. When air is allowed rapidly to enter a gas-holder containing the gas, white fumes are at once formed, and these increase in quantity with the amount of air until, when a certain volume has been introduced, a sharp explosion takes place accompanied by light and heat, and the mercury is forcibly ejected from the cylinder. When a quantity of thiophosphoryl fluoride is passed into **oxygen** contained in a eudiometer standing over mercury, the fluoride, being about four times heavier than the oxygen, collects on the surface of the mercury, and burns quietly with a yellow flame, and a white fume is produced which quickly settles on the sides of the eudiometer. If the oxygen is passed into the gas, combination is more rapid, and a much denser deposit settles. When, however, the gas is gradually passed into the oxygen, that is, in a slow stream of small bubbles, the behaviour of the two gases is considerably altered. The first few bubbles on reaching the oxygen inflame, giving a blue flash of light. As oxidation products collect on the surface of the mercury, more bubbles may be added without any signs of combination until when a certain amount of gas has accumulated in the oxygen, a bright yellow flash is seen to traverse the gaseous mixture, and is followed by a smart detonation. Dry oxygen and thiophosphoryl fluoride may in fact exist together in presence of a sufficient quantity of oxidation products, apparently without interaction, provided all traces of moisture are carefully excluded from the mixture. The gas can be mixed with excess of dry oxygen without the slightest change taking place, even when the eudiometer is gently heated. The mixture, however, at once inflames on exposure to the air. That it is the moisture in the air which serves to start the reaction is proved by the fact that on passing fragments of blotting-paper moistened with water into the mixture of gas and oxygen their explosive union instantly follows. The reaction is not in accord with the equation: $2PSF_3+3O_2=2POF_3+2SO_2$; but a portion of the gas is acted on by oxygen: $PSF_3+O_2=PF_3+SO_2$; and the resulting trifluoride reacts with oxygen: $10PF_3+5O_2=6PF_5+2P_2O_5$, and $2PF_3+O_2=2POF_3$, so that the resultant equation is $10PSF_3+15O_2=6PF_5+2P_2O_5+10SO_2$. On introducing a flame of thiophosphoryl fluoride burning in air into an atmosphere of oxygen, the flame is reduced in size and becomes much more luminous. Its colour changes from greyish-green to bright yellow, and dense, white fumes are given off. The soln. of the products formed smells strongly of sulphur dioxide, and gives the reactions of phosphoric acid. Thiophosphoryl fluoride cannot be burned with safety from a jet in a closed apparatus through which a current of dry air or oxygen is passing. The flame is liable to be extinguished by a current of air or oxygen sufficiently powerful to carry over the products into the absorption-tubes. As a rule, the gas speedily relights itself, but not before sufficient unburnt gas has escaped to form a spontaneously explosive mixture. Two attempts were made to burn the gas in a closed space, and in each case the apparatus was shattered by explosion. These results illustrate the extreme instability of the gas and its low ignition temp. From the low ignition temp., and the ease with which the flame is extinguished, the temp. of the latter is very low. It is probably one of the coldest flames known. Our hands have frequently been surrounded by it without any too inconvenient sensation of heat. If a stream of thiophosphoryl fluoride is passed through **water,** comparatively little of the gas is absorbed. The bubbles rise to the surface, and take fire immediately on reaching the air, forming rings of white smoke. In order that any appreciable quantity may be dissolved, the gas must be shaken with the water for some time. The soln. is acid to test-paper, smells of hydrogen, and gives the reactions for phosphoric and hydrofluoric acids. The decomposition is in accordance with the equation: $PSF_3+4H_2O=H_2S+H_3PO_4+3HF$. If the soln. is effected in a vessel of flint-glass, the liquid at once becomes black, owing to the action of the hydrofluoric acid and hydrogen sulphide upon the lead silicate. The decomposition of thiophosphoryl fluoride by a soln. of **alkali hydroxide,** is analogous to that which C. A. Wurtz observed with thiophosphoryl chloride: $PSF_3+6NaOH=Na_3PSO_3+3NaF+3H_2O$. Thiophosphoryl fluoride has no action on **sulphuric acid.** If **ammonia** gas be passed into a confined vol. of thiophosphoryl fluoride, the two gases combine with the evolution of heat and the formation of a white solid. The volume ratios agree with the assumption that *thiophosphoryl diamidofluoride,* $P(NH_2)_2SF$, is formed: $PSF_3+4NH_3=2NH_4F+P(NH_2)_2SF$. Thiophosphoryl fluoride has no action on **carbon disulphide,** or **benzene**; it dissolves in **ether,** and the soln. burns with a greenish flame. Neither the gas nor the liquid has any appreciable action on dry **glass** at ordinary temp., but when heated with glass, a yellow film is deposited on the glass: $PSF_3=PF_3+S$, followed by $4PF_3+3SiO_2=3SiF_4+4P+3O_2$. A portion of the phosphorus combines with sulphur, whilst another part is oxidized and unites with the bases of the glass, forming pyrophosphates or metaphosphates. The deposit on the extreme upper part of the tube is yellow, and inflames on being heated in the air; it dissolves in water with separation of a little silica, and the soln. smells of sulphuretted hydrogen, and gives the reactions for phosphoric acid. If thiophosphoryl fluoride be passed over heated **sodium,** the metal takes fire and burns with a red flame, and the residual mass, when treated with water, gives off spontaneously inflammable phosphine. The gas has no action on **mercury.** The gas is completely absorbed by **lead dioxide.**

A number of compounds of phosphorus, sulphur, and chlorine have been reported, namely, the normal thiophosphoryl chloride, $PSCl_3$; **phosphorus dithiopentachloride,** PS_2Cl_5, reported by J. H. Gladstone,[2] and E. Baudrimont to be formed by melting a mixture of phosphorus pentachloride and sulphur, and fractionally distilling at 125°, the liquid remaining after the crystals of mixed phosphorus pentachloride and thiophosphoryl chloride have separated out. C. F. Gerhardt considered the product to be a mixture of thiophosphoryl chloride and sulphur monochloride, but E. Baudrimont could not separate it by fractional distillation. According to J. H. Gladstone, the pale yellow, mobile, refracting liquid is heavier than water. Its vap. density is 5·5, air unity. It evaporates at ordinary temp., boils at 118°, and does not freeze at —17°. It is affected by hydrogen at the b.p. of the liquid; it reacts slowly with water,forming hydrochloric, sulphuric, and phosphoric acids; it forms a dark red liquid with alkali-lye, and sulphur separates out. The liquid dissolves iodine, and sulphur. It dissolves hydrogen sulphide with the separation of sulphur; it is attacked by nitric acid; it dissolves phosphorus, and phosphorus pentachloride; it mixes with carbon disulphide; and it attacks alcohol, ether, and turpentine; it is also decomposed by metals—hot or cold.

H. Rose said that **phosphorus pentathiodichloride**, PS_5Cl_2, is formed by the action of phosphine on sulphur monochloride: $5S_2Cl_2+2PH_3=2PS_5Cl_2+6HCl$. The yellow, syrupy liquid is decomposed by water with the separation of sulphur and the evolution of hydrogen sulphide; and it is oxidized by nitric acid to sulphuric and phosphoric acids.

G. S. Sérullas[3] first made **thiophosphoryl chloride**, $PSCl_3$, by the action of hydrogen sulphide on phosphorus pentachloride: $PCl_5+H_2S=2HCl+PSCl_3$; L. Carius, B. Rathke, and A. W. Hofmann used carbon disulphide as the source of the sulphur: $CS_2+2PCl_5=CCl_4+2PSCl_3$; R. Weber, and T. E. Thorpe, phosphorus tetritadecasulphide; $P_4S_{10}+6PCl_5=10PSCl_3$, in a sealed tube at 150°; H. Schiff, potassium thiocyanate: J. Ponomareff, perthiocyanic acid; E. Baudrimont, sulphur, or antimony trisulphide: $3PCl_5+Sb_2S_3=2SbCl_3+3PSCl_3$; R. Weber, and E. Baudrimont, metal sulphides; A. Michaelis, thiophosphoryl bromide: $5PSBr_3+PCl_5=5PSCl_3+3PBr_5$; and C. F. Gerhardt, organic sulphur compounds. L. Henry made the compound by heating at about 130° in a sealed tube a mixture of a mol of phosphorus trichloride and a gram-atom of sulphur. A. Michaelis noted the formation of this compound when a mixture of phosphorus trichloride is heated with sulphur monochloride in a sealed tube at 160°—if thionyl chloride be employed some phosphoryl chloride is formed at the same time. F. Wöhler made it by heating sulphur monochloride with phosphorus: $2P+3S_2Cl_2=2PSCl_3+4S$. M. Chevrier added the phosphorus in small pieces at a time to the boiling sulphur monochloride, and the soln. of sulphur in thiophosphoryl chloride was fractionally distilled at 125°. A. von Flemming agitated the liquid with a little water before the rectification. T. E. Thorpe and A. E. H. Tutton heated sulphur monochloride with phosphorous oxide: $P_4O_6+6S_2Cl_2=2PSCl_3+2POCl_3+8S+2SO_2$; A. Besson, thionyl chloride and phosphine; H. Prinz, thionyl chloride and phosphorus tetritadecasulphide at 100°–150° in a sealed tube: $6SOCl_2+P_4S_{10}=4PSCl_3+3SO_2+9S$; L. Carius, phosphoryl chloride with phosphorus tetritadecasulphide, at 150°; and E. Baudrimont, thiophosphoryl bromide with chlorine, or by heating thiophosphoryl chlorodibromide or dichlorobromide: $2PSCl_2Br=PSCl_3+PSClBr_2$; E. Glatzel, by heating metal chlorides with phosphorus tetritadecasulphide: $3MCl+P_2S_5=M_3PS_4+PSCl_3$, and with ferric chloride: $6FeCl_3+2P_2S_5=3FeCl_2+3FeS_2+4PSCl_3$.

Analyses by G. S. Sérullas, L. Carius, and A. von Flemming are in agreement with the formula $PSCl_3$; and the vap. density determinations of A. Cahours, and M. Chevrier, 5·963 at 168°, and 5·878 at 298°, are in agreement with the same formula. The mol. wt. calculated from the b.p. of soln. of thiophosphoryl chloride in carbon tetrachloride is 209; and in benzene, 241; and from the f.p. of soln. in benzene, 160. The value calculated for $PSCl_3$ is 169·5, and for $(PSCl_3)_2$, 339. T. E. Thorpe said that the physical properties are in agreement with the assumption that the phosphorus is tervalent, and hence supposes the constitution to be $Cl_2P—S—Cl$; but W. Ramsay said that this evidence is of little weight—*vide* phosphoryl chloride. A. M. Wasilieff said that it can be regarded as a eutectic $P_2S_5+3PCl_5$, but the meaning of the term is not that usually employed.

G. S. Sérullas, E. Baudrimont, and L. Henry described thiophosphoryl chloride as a transparent, colourless, mobile liquid with a characteristic pungent and aromatic odour. The liquid fumes in air, and the smell of hydrogen sulphide indicates that it has been hydrolyzed by the moisture of the air. E. Baudrimont found the sp. gr. to be 1·631 at 22°; M. Chevrier, 1·636 at 22°; and T. E. Thorpe, 1·66816–1·66820 at 0° and 1·45599 at 125·12°. O. Masson, and J. A. Groshans studied the mol. vols.

of the family of halides. According to T. E. Thorpe, unit vol. of the liquid occupies v vols. at 0° when

	0°	20°	40°	60°	80°	100°	120°	125°
v . .	1·00000	1·02019	1·04129	1·06348	1·08695	1·11187	1·13842	1·14534

or $v=1+0{\cdot}0_3 99011\theta+0{\cdot}0_6 9030\theta^2+0{\cdot}0_8 3825\theta^3$. The mol. vol. at the b.p. is 116·34; and the at. vol. of the contained phosphorus is 52·4. G. S. Sérullas gave 125° for the b.p. of the liquid: L. Henry, 125°–126°; A. Cahours, 126°–127°; M. Chevrier, 124·5° at 750°; E. Baudrimont, 124·25°; T. E. Thorpe, 126° at 770 mm.; 125° and 125·12° at 760 mm. A. Besson found that the liquid freezes to a white solid when cooled in a bath of methyl chloride; he gave —35° for the m.p.; and added that the liquid is easily undercooled but it is readily crystallized by seeding with a crystal of thiophosphoryl dichlorobromide, or chlorodibromide. M. Chevrier gave 1·5593 for the refractive index of the liquid for Na-light. R. Weber found that the liquid is not decomposed by the electric current; and P. Walden gave 5·8 for the dielectric constant at 21·5°.

According to M. Chevrier, the vapour of thiophosphoryl chloride decomposes when passed through a red-hot tube, forming sulphur monochloride, phosphorus trichloride, and sulphur; and it is explosive when admixed with **oxygen.** G. S. Sérullas, and L. Henry observed that the liquid sinks in **water,** and is slowly decomposed in a few days, forming hydrochloric and phosphoric acids, hydrogen sulphide, and maybe a little sulphur which makes the soln. turbid. The liquid is decomposed in a few hours if it be agitated with water. G. Carrara and I. Zoppelari studied the speed of decomposition of the heterogeneous system, and represented the results by $\log \{a/(a-x)\}=Stak$, where S denotes the surface area of the two liquids in contact; a, the quantity of decomposable liquid; x, the amount of liquid decomposed at the time t; and k, a constant 0·0000132 at 10°, and 0·0000238 at 30°. E. Baudrimont found that it reacts with **chlorine,** forming sulphur monochloride and phosphorus pentachloride, and M. Chevrier represented the reaction: $PSCl_3+3Cl_2=SCl_4+PCl_5$; **iodine,** said C. A. Wurtz, does not react with thiophosphoryl chloride. According to A. Besson, dry **hydrogen bromide** does not react with boiling thiophosphoryl chloride; but when a mixture of the vapours is passed over pumice-stone at 400°–500°, a mixture of thiophosphoryl bromide, chlorodibromide, and dichlorobromide is formed; **hydrogen iodide** dissolves in liquid thiophosphoryl chloride at 0°, and the soln. darkens in colour owing to the reaction: $PSCl_3+5HI=PI_3+I_2+H_2S+3HCl$, and if the soln. be warmed phosphorus triiodide, phosphorus tetritahexa- and tetritadeca-sulphides, and phosphorus thiodiiodide are formed. G. S. Sérullas observed that hot liquid thiophosphoryl chloride dissolves **sulphur,** most of the solute separates out on cooling, and remains behind when the soln. is distilled. When a mixture of the vapour of thiophosphoryl chloride and **hydrogen sulphide** is passed through a red-hot tube, E. Baudrimont observed that hydrogen chloride, and phosphorus tetritadecasulphide are formed. When thiophosphoryl chloride is exposed to dry **ammonia** gas, heat is evolved, and a white solid is formed containing, according to E. Baudrimont, 30–40 per cent. of ammonia; or, according to J. H. Gladstone and J. D. Holmes, 60 per cent. J. H. Gladstone and J. D. Holmes represented the reaction as forming *thiophosphoryl diamidochloride*: $PSCl_3+4NH_3=2NH_4Cl+P(NH_2)_2ClS$; while H. Schiff, and M. Chevier assumed that thiophosphoryl triamide is formed: $PSCl_3+6NH_3=3NH_4Cl+PS(NH_2)_3$. G. S. Sérullas said that an aq. soln. of ammonia behaves like water, but J. H. Gladstone and J. D. Holmes said that ammonium monamidomonothiophosphate is formed; and, added M. Chevrier, if the ammonia is in excess, ammonium thiophosphate is produced. G. S. Sérullas found that **phosphorus** dissolves in warm thiophosphoryl chloride, but most of the solute separates out on cooling, and remains behind when the liquid is distilled; but F. Wöhler observed that when the liquid is distilled with phosphorus some phosphorus trichloride and sulphide are formed. A. Besson said that he was unable to prove the formation of phosphorus thiodiiodide when thiophosphoryl chloride is heated with **phosphonium iodide**; T. E. Thorpe and J. W. Rodger found that in a sealed tube at 150°, **arsenic trifluoride** forms thiophosphoryl fluoride (*q.v.*). According to E. Baudrimont, thiophosphoryl chloride dissolves **iodoform,** and mixes with **carbon disulphide.** S. Cloez found that thiophosphoryl chloride reacts vigorously with methyl or ethyl **alcohol**: $PSCl_3+3C_2H_5OH=(C_2H_5)H_2PSO_3+2C_2H_5Cl+HCl$, and slowly with amyl alcohol; it also reacts with **sodium ethoxide**: $3C_2H_5ONa+PSCl_3=(C_2H_5)_3PSO_3+3NaCl$.

Metals do not act on thiophosphoryl chloride in the cold. According to M. Chevrier, **sodium** and **potassium** are not attacked by boiling thiophosphoryl chloride, but if the chloride be dropped on the molten metal, the formation of alkali chloride, and sulphide, and sulphur is accompanied by an explosion; heated **mercury** forms mercuric chloride and a little phosphorus and sulphur. G. S. Sérullas said that alkali-lye acts like water; and, according to C. A. Wurtz, and S. Cloez, **sodium hydroxide** forms sodium monothiophosphate and sodium chloride, and, added M. Chevrier, some sulphur and sodium phosphate are produced; the last-named found that copper hydroxide acts in a similar manner, and that **silver oxide,** and red **mercuric oxide,** act when warmed, while yellow mercuric oxide acts in the cold. According to E. Baudrimont, **mercuric sulphide,** and **antimony trisulphide,** react at a red-heat, forming the corresponding chloride and thiophosphide. M. Chevrier found that **potassium permanganate** is decolorized with the separation of manganese dioxide; and T. E. Thorpe and S. Dyson represented the reaction with **silver nitrate**: $PSCl_3+4AgNO_3=Ag_3PO_4+AgCl+SO_2+2NOCl+N_2O_4$, and some pyrosulphuryl nitrate is formed.

Three thiophosphoryl bromides have been reported, $PSBr_3$, $P_2S_3Br_4$, P_2SBr_6, and PS_2Br, as well as the mixed chlorobromides, $PSBr_2Cl$, and $PSBrCl_2$. A. Stock[4] also reported that when dry hydrogen bromide acts on ammonium trithiophosphate some **thiophosphoryl hydrosulphodibromide,** $PSBr_2(SH)$, is formed, along with normal thiophosphoryl bromide. J. H. Gladstone first prepared **thiophosphoryl bromide,** $PSBr_3$, without recognizing its true nature. He obtained it by the action of hydrogen sulphide on phosphorus pentabromide, and E. Baudrimont showed that the reaction is that symbolized by $PBr_5+H_2S=PSBr_3+2HBr$. The product of this reaction, said R. W. E. MacIvor, is always mixed with some undecomposed pentabromide, which may be removed by washing the product with water at about 45°; and dried by pressure between bibulous paper, and finally in a desiccator over conc. sulphuric acid. A. Michaelis recommended removing the water by dissolving the product in carbon disulphide, dehydrating the soln. by calcium chloride, and evaporating the solvent from the clear, decanted liquor. E. Baudrimont obtained the same compound by the action of phosphorus pentabromide on heated antimony trisulphide; and by distilling a mixture of phosphorus tribromide with sulphur. The accompanying phosphorus bromide is removed by washing with warm water. A. Michaelis obtained it by the action of bromine on a soln. of eq. proportions of phosphorus and sulphur in carbon disulphide; by decomposing thiopyrophosphoryl bromide with water; and by heating hydrated thiophosphoryl bromide to its m.p. A. Besson obtained it by passing the vapour of thiophosphoryl chloride and hydrogen bromide over pumice-stone at 400°–500°, and by heating thiophosphoryl chlorodibromide. T. E. Thorpe proposed to prepare it by heating phosphorus pentabromide and tetritadecasulphide: $3PBr_5+P_2S_5=5PSBr_3$, as with the corresponding chloride. A. Stock obtained it, as indicated above, by treating ammonium trithiophosphate with anhydrous hydrogen bromide, digesting the yellow oil with water, and isolating the thiophosphoryl bromide by the carbon disulphide process just indicated. The analyses of A. Michaelis, E. Baudrimont, and A. Stock are in agreement with the formula $PSBr_3$.

E. Baudrimont described this compound as "a yellow, thick mass with a disgusting smell"; but A. Michaelis obtained it in octahedral crystals belonging to the cubic system by evaporation of the soln. in carbon disulphide, or phosphorus tribromide. A yellow, crystalline mass is obtained by cooling the molten compound, and it has a pungent, aromatic odour. The vapour attacks the eyes. E. Baudrimont gave 2·72 for the sp. gr.; A. Michaelis, 2·85 at 17°; and R. W. E. MacIvor, 2·87. For the m.p., E. Baudrimont gave 39°; A. Michaelis, and A. Stock, 38°; and R. W. E. MacIvor, 36·4°. The yellow liquid is readily undercooled. E. Baudrimont said that the liquid becomes brown when heated, and at 175°, a greenish vapour appears, and on distillation, phosphorus tribromide is first given off; this is followed by thiophosphoryl bromide at 212°–215°, while sulphur and phosphorus sulphide remain in the retort.

E. Baudrimont said that thiophosphoryl bromide fumes in **air,** but it does not burn in air. It is decomposed by **water,** forming hydrobromic and phosphoric acids, hydrogen sulphide, and sulphur. A. Michaelis, and R. W. E. MacIvor found that the reaction with water is very slow even when the water is boiling, and in addition to the products indicated by E. Baudrimont, some phosphorus acid is formed. For *hydrated thiophosphoryl bromide,* $PSBr_5H_2O$, *vide infra.* E. Baudrimont said that the thiobromide dissolves **sulphur,** and it is turbulently decomposed by conc. **nitric acid.** A. Michaelis found that thiophosphoryl bromide is slowly decomposed by **ammonia** in the cold, but rapidly when heated, forming sulphur, and ammonium sulphide, hydrophosphite, and phosphate. He represented the reaction with **phosphorus pentachloride :** $5PSBr_3+3PCl_5=5PSCl_3+3PBr_5$. The compound is soluble in **phosphorus trichloride,** and in **phosphorus tribromide ;** A. Michaelis, and R. W. E. MacIvor found that thiophosphoryl bromide dissolves in **ether,** and **carbon disulphide ;** and, added E. Baudrimont, in **chloroform.** It reacts when heated with **alcohol,** forming, according to A. Michaelis, ethyl thiophosphate, $PS(OC_2H_5)_3$. E. Baudrimont said that thiophosphoryl bromide is turbulently decomposed by **potassium hydroxide** soln.

A. Michaelis reported that when thiophosphoryl bromide is slowly distilled **thiopyrophosphoryl hexabromide,** P_2SBr_6, is formed. The same compound is formed by distilling thiopyrophosphoryl tetrabromide at 205°. It melts at —5°; and boils with decomposition at 205°. If this substance be stirred up with water, a yellow oil is formed which slowly crystallizes. It can be dried by press. between bibulous paper, and finally over conc. sulphuric acid and potassium hydroxide. The composition corresponds with hydrated thiopyrophosphoryl bromide, and it can be dehydrated by dissolving it in carbon disulphide, and agitation of the soln. with calcium chloride as indicated above. The yellow, crystalline mass has an aromatic smell. Its sp. gr. is 2·7937 at 18°, and it fuses at 35°. The water is gradually lost at the m.p. It does not fume in air, but after some days, it is gradually decomposed in air giving off hydrogen bromide.

According to A. Michaelis, **thiopyrophosphoryl tetrabromide,** $P_2S_3Br_4$, or $PSBr_2.S.PSBr_2$, is formed by gradually adding, with constant agitation, a carbon disulphide soln. of bromine to a well-cooled mixture of phosphorus tetritahexasulphide and the same menstruum. The solvent is distilled off at a temp. not exceeding 80°, and the last traces are removed by a current of dry carbon dioxide. The oily liquid is purified by dissolving it in ether, and distilling the solvent from the clear liquid. The pale yellow oil has a sp. gr. 2·2621 at 17°. It fumes in air, and then deposits sulphur. It has a pungent, aromatic odour. It cannot be distilled without decomposition into sulphur, phosphorus tetritadecasulphide, and thiopyrophosphoryl hexabromide. It is decomposed by water into sulphur, thiophosphoryl bromide, hydrogen sulphide, and phosphoric and thiophosphoric acids. Alkali-lye acts like water, only the reaction is more violent and no sulphur or thiophosphoryl bromide is formed; phosphorus pentabromide forms thiophosphoryl bromide; and alcohol forms $P_2S_3(OC_2H_5)_3Br$, $P_2S_3(OC_2H_5)_4$, and $P_2S_3(OC_2H_5)_2(SC_2H_5)_2$.

According to A. Michaelis, in the preparation of pyrophosphoryl tetrabromide, the crude product is extracted with ether, and there remains a yellow, viscid mass which can be dissolved in carbon disulphide. The solvent can be expelled from the filtered soln. by means of a current of carbon dioxide. The product is impure **thiometaphosphoryl bromide,** PS_2Br. It is decomposed by water, and reacts with alcohol, forming crystals of $P_2S_3(OC_2H_5)_2(SC_2H_5)_4$.

A. Besson[5] prepared **thiophosphoryl chlorodibromide,** $PSClBr_2$, along with the dichlorobromide and the normal bromide by passing a mixture of dry hydrogen bromide and thiophosphoryl chloride vapour over pumice-stone at 400°–500°, and separating the products by fractional distillation under reduced press. It is also obtained by heating thiophosphoryl dichlorobromide in a sealed tube at 100°: $2PSCl_2Br=PSClBr_2+PSCl_3$. The very pale green, fuming liquid has a sp. gr. 2·48 at 0°; and it forms a white solid with the m.p. —60°. It boils at 95° and 60 mm. press.; it slowly decomposes if heated at ordinary press.; and in a sealed tube at 100°, it decomposes into thiophosphoryl chloride, bromide, and dichlorobromide. It is slowly decomposed by water, and behaves towards other reagents like the dichlorobromide.

A. Michaelis prepared **thiophosphoryl dichlorobromide,** $PSCl_2Br$, by slowly adding bromine to ethyl thiophosphoryldichloride, $P(SC_2H_5)Cl_2$, in equimolar proportions: $P(SC_2H_5)Cl_2+Br_2=PSCl_2Br+C_2H_5Br$. The ethyl compound is obtained by adding mercaptan to phosphorus trichloride in equimolar proportions, and collecting the fraction boiling at 172°–175°. The crude dichlorobromide was shaken with water so long as a perceptible action occurs, dried by calcium chloride, and freed from dissolved hydrochloric and hydrobromic acids by gently warming. A. Besson obtained it as indicated above, and also by heating thiophosphoryl chlorodibromide in a sealed tube at 100°, and isolating the desired product by fractional distillation. A. Besson, and A. Michaelis said that the pale yellow or colourless liquid smells like thiophosphoryl chloride. A. Besson gave 2·12 for the sp. gr. at 0°; and when cooled, it forms a white solid melting at —30°. The liquid is readily undercooled, and the surfused liquid readily crystallizes when seeded with a crystal of thiophosphoryl dichlorobromide or chlorodibromide. A. Michaelis found that the liquid cannot be distilled at atm. press. without decomposition; A. Besson said that it decomposes at 100° in a sealed tube: $2PSCl_2Br=PSCl_3+PSClBr_2$, but he was able to distil the liquid at 80° and 60 mm. press. A. Michaelis said that the compound is acted upon by water only with difficulty, and may even be partially distilled in a current of steam. Its complete decomposition is effected only by heating in sealed tubes to 150°. The products are sulphur, hydrogen sulphide, phosphorus, phosphoric, hydrochloric, and hydrobromic acids. Only half as much sulphur, however, is obtained as in the analogous decomposition of $PSBr_3$ by water. A. Besson added that the dichlorobromide is boiled at about 80° under a press. of 6 mm.; sp. gr.=2·12 at 0°. When strongly cooled, it forms a white solid, which melts at 30°. It decomposes slowly in presence of water, more rapidly in contact with soln. of alkalies. Fuming nitric acid oxidizes it violently, but the acid at 36° acts more slowly, and completely oxidizes the sulphur and phosphorus. When heated at 100°, it decomposes into the thiophosphoryl trichloride and the chlorodibromide, the latter, in its turn, decomposing and yielding, amongst other products, thiophosphoryl tribromide.

A number of **phosphorus thioiodides** have been reported: P_2SI_2, $P_2S_2I_2$, P_2SI_4, and $P_4S_3I_2$; but their individuality is not well-established. The subject needs revision. Another compound was prepared by V. Auger[6] by mixing carbon disulphide soln. of phosphorus triiodide and sulphur. The reddish-brown crystals were stated by M. Demassieux to be rhombohedral. They were not obtained pure enough for analysis, but by analogy with the corresponding compounds of arsenic and antimony triiodides, their composition is $PI_3.3S_8$, or **phosphorus tetracosithiotriiodide.**

According to A. Besson, hydrogen iodide dissolves without change in thiophosphoryl chloride cooled in a mixture of ice and salt, but at 0° hydrogen chloride and hydrogen sulphide are given off, and the liquid contains free iodine and phosphorus triiodide, the action being analogous to that of hydrogen iodide on phosphorus oxychloride. In sealed tubes at temperatures above 0°, the reaction is more complex, and the products depend on the temperature. In all cases, iodine is liberated, hydrogen chloride and sulphur are given off, and the liquid contains phosphorus triiodide and a mixture of phosphorus trisulphide and pentasulphide in varying proportions, together with small quantities of **phosphorus thiodiiodide,** P_2SI_2, an orange solid, which melts at about 75°, and is very soluble in carbon disulphide. The thioiodide does not sublime in a vacuum, decomposes when exposed to air, and readily when heated. In order that it may be formed in appreciable quantity, the soln. of hydrogen iodide in the thiophosphoryl chloride must not be heated above 30°–40°.

E. Drechsel reported a product with the empirical formula PSI to be formed by the action of carbon disulphide on phosphonium iodide: $3CS_2+4PH_4I=3PSI+P(CH_3)_3.HI+3H_2S$; and L. Ouvrard showed that while dry hydrogen sulphide has no action on phosphorus triiodide at ordinary temp., **phosphorus dithiodiiodide,** $P_2S_2I_2$, is produced when the dry gas is passed over the molten iodide: $2PI_3+2H_2S=P_2S_2I_2+4HI$. The same compound is produced when the required proportions of the three elements in carbon disulphide soln. are heated in the absence of air, and the solvent evaporated; by heating the triiodide with phosphorus tetritahexasulphide in an inert gas: $2P_2S_3+2PI_3=3P_2S_2I_2$; and by the action of iodine on a soln. of the same sulphide in carbon disulphide: $2P_2S_3+3I_2=S_2I_2+2P_2S_2I_2$. The red, prismatic crystals are readily decomposed in air with the formation of hydrogen iodide; they inflame when heated in air, burn to sulphur dioxide, iodine, etc.; they are decomposed by water into hydriodic and phosphoric acids, and phosphorus tetritahexasulphide which, in turn, is resolved into phosphoric acid, hydrogen sulphide, etc. The dithiodiiodide is readily dissolved by carbon disulphide.

L. Ouvrard said that when an excess of phosphorus triiodide acts on phosphorus tetritahexasulphide, **phosphorus thiotetraiodide,** P_2SI_4, is formed: $P_2S_3+4PI_3=3P_2SI_4$. It is readily decomposed on recrystallization from carbon disulphide: $3P_2SI_4=P_2S_3+4PI_3$, and appears to be more stable in soln. L. Ouvrard also reported **phosphorus trithiodiiodide,** $P_4S_3I_2$, to be formed by the action of dry hydrogen sulphide on phosphorus diiodide at 110°–120°: $2P_2I_4+3H_2S=6HI+P_4S_3I_2$, until no more hydrogen iodide is given off. The reaction is very slow, and occupies 40–50 hrs. The product is extracted with carbon disulphide, and the filtered soln. evaporated in a current of carbon dioxide. The same compound is formed when the correct proportions of the three elements are dissolved in carbon disulphide, and after the evaporation of the solvent, heating the product to 120° in a current of an inert gas. It is also formed when the correct proportion of iodine is dissolved in a carbon disulphide soln. of phosphorus tetritatrisulphide. L. Wolter added that no other phosphorus sulphide yields a well-defined iodide under these conditions, and he recommended the reaction as a test for the tetritatrisulphide in match composition. L. Wolter described the trithiodiiodide as crystallizing from carbon disulphide in orange-yellow, silky needles; and L. Ouvrard, as highly refractive, golden-yellow prisms belonging to the triclinic system. L. Wolter gave 119·5° for the m.p.; and L. Ouvrard said that when heated in air, the trithiodiiodide melts at about 106° to a viscous liquid which easily remains in a state of surfusion, and at about 300°, it burns, forming phosphorus pentoxide, sulphur dioxide, and iodine; and at 300° in vacuo, it forms iodine and phosphorus tetritatrisulphide. It is stable in dry air, and can be preserved for a long time in a closed vessel; it is slowly decomposed by moist air with the evolution of hydrogen sulphide. Cold water has very little effect on it, but it is rapidly decomposed by boiling water. Fuming nitric acid attacks it with explosive violence and the evolution of light. It dissolves readily in carbon disulphide, and is only slightly soluble in benzene, xylene, toluene, chloroform, ligroin, and acetic acid. It is still less soluble in absolute alcohol and ether. The soln. in hot ether yield crystals of the same compound on cooling.

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